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(71)Applicant : FUJI PHOTO FILM CO LTD

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(72)Inventor : NAKAO HAJIME
SATO KENICHIRO

(54) POSITIVE TYPE PHOTORESIST COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a positive type photoresist composition which reduces the occurrence of development defects in the production of a semiconductor device, is free from particles generated in the dissolution of solid components in a solvent and prevents the occurrence of particles in storage and the variation of sensitivity due to storage.

SOLUTION: The positive type photoresist composition contains a resin containing specified repeating structural units and having a velocity of dissolution in an alkali developing solution increased by the action of an acid, a compound which generates the acid when irradiated with active light or radiation and a specified mixed solvent.

LEGAL STATUS

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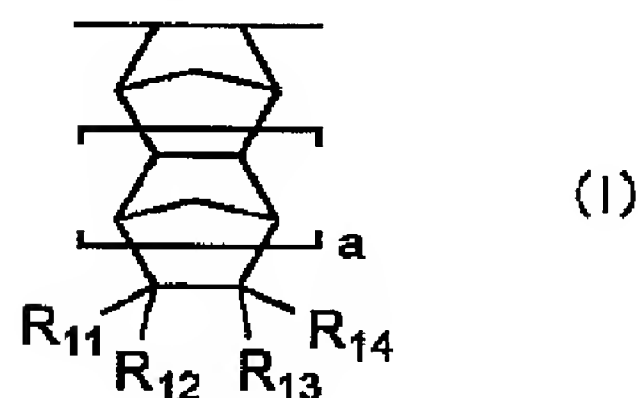
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CLAIMS

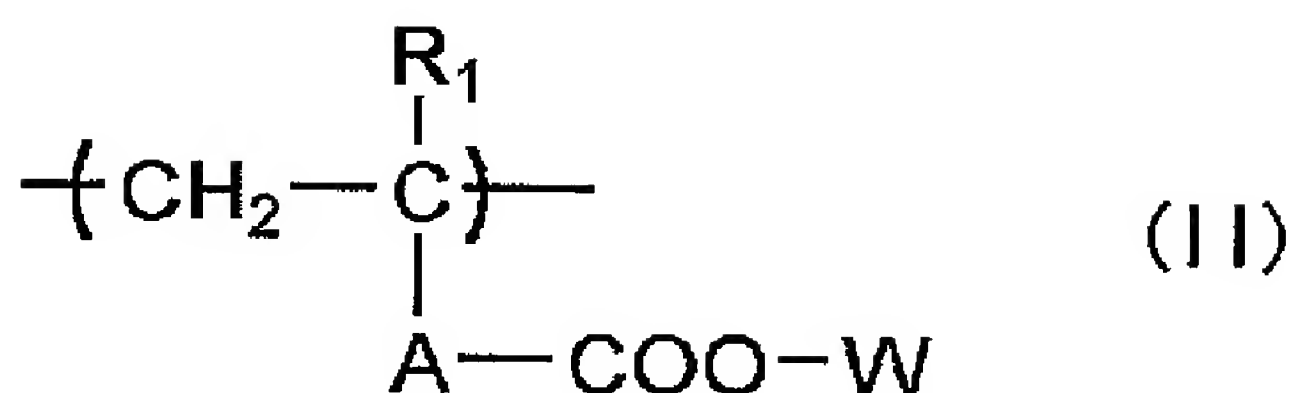
[Claim(s)]

[Claim 1] (A) Contain the repeat structural unit shown by the repeat structural unit shown by the following general formula (I), and the following general formula (II). The compound which generates an acid by the exposure of the resin which the dissolution rate to an alkali developer increases according to an operation of an acid, (B) activity beam of light, or a radiation, And the partially aromatic solvent containing at least one sort chosen from a (C) following solvent A group, and at least one sort chosen from a following solvent B group, Or the partially aromatic solvent A group:chain-like ketone B group containing at least one sort chosen from a following solvent A group, and at least one sort chosen from a following solvent C group : Lactic-acid alkyl, Alkoxy alkyl propionate, acetic ester, and a propylene-glycol monoalkyl-ether C group: The positive type photoresist constituent characterized by containing gamma-butyrolactone, ethylene carbonate, and propylene carbonate.

[Formula 1]



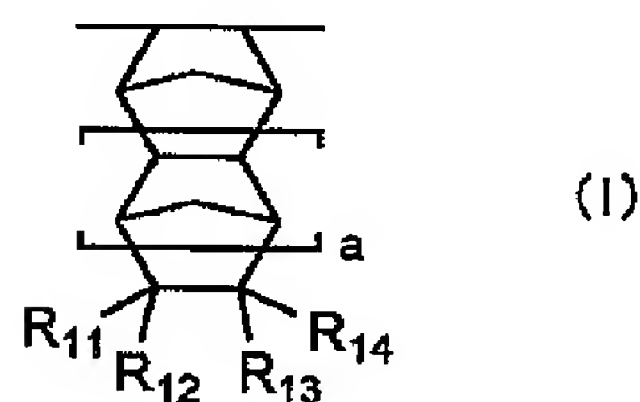
[Formula 2]



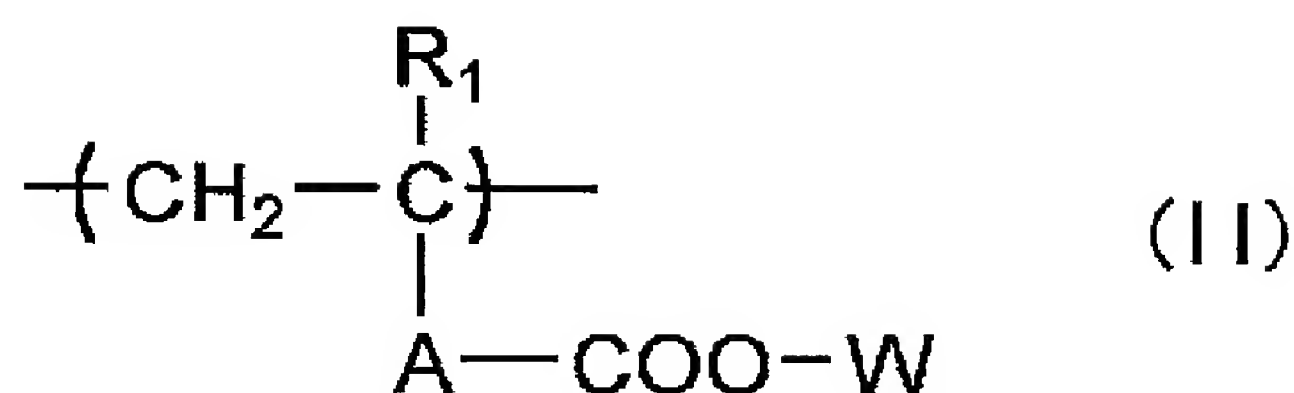
R11-R14 express the alkyl group which may have a hydrogen atom or a substituent independently respectively among a general formula (I). a is 0 or 1. R1 expresses a hydrogen atom or a methyl group among a general formula (II). A expresses the combination of independent [which is chosen from the group which consists of single bond, an alkylene group, a cyclo alkylene group, a ether group, a thioether radical, a carbonyl group, and an ester group], or two radicals or more. W expresses the radical expressed with the radical or -CH(Rd)-O-Re expressed with -C (Ra), (Rb), and (Rc). Here, Ra, Rb, and Rc express respectively the shape of a straight chain of one ~ 20 carbon numbers which may have a halogen atom, the alkoxy group, the alkoxy carbonyl group, the acyl group, or the acyloxy radical as a substituent, the letter alkyl group of branching, or the cycloalkyl radical of 3-20 carbon numbers. However, it may join together mutually and Ra and Rb may form an alicyclic monocycle. A hydrogen atom or an alkyl group is expressed as Rd. As Re, the shape of a straight chain of one ~ 20 carbon numbers which may have a halogen atom, the alkoxy group, the alkoxy carbonyl group, the acyl group, or the acyloxy radical as a substituent, the letter alkyl group of branching, or the cycloalkyl radical of 3-20 carbon numbers is expressed.

[Claim 2] (A) Contain the repeat structural unit shown by the repeat structural unit shown by the following general formula (I), and the following general formula (II). The compound which generates an acid by the exposure of the resin which the dissolution rate to an alkali developer increases according to an operation of an acid, (B) activity beam of light, or a radiation, And at least one sort chosen from a (C) following solvent A group, at least one sort chosen from a following solvent B group, And the partially aromatic solvent A group: chain-like ketone B group containing at least one sort chosen from a following solvent C group : Lactic-acid alkyl, Alkoxy alkyl propionate, acetic ester, and a propylene-glycol monoalkyl-ether C group: The positive type photoresist constituent characterized by containing gamma-butyrolactone, ethylene carbonate, and propylene carbonate.

[Formula 3]



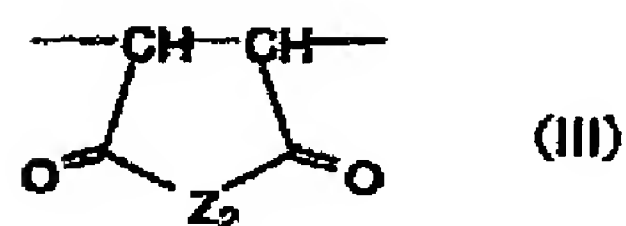
[Formula 4]



R11-R14 express the alkyl group which may have a hydrogen atom or a substituent independently respectively among a general formula (I). a is 0 or 1. R1 expresses a hydrogen atom or a methyl group among a general formula (II). A expresses the combination of independent [which is chosen from the group which consists of single bond, an alkylene group, a cyclo alkylene group, a ether group, a thioether radical, a carbonyl group, and an ester group], or two radicals or more. W expresses the radical expressed with the radical or -CH(Rd)-O-Re expressed with -C (Ra), (Rb), and (Rc). Here, Ra, Rb, and Rc express respectively the shape of a straight chain of one - 20 carbon numbers which may have a halogen atom, the alkoxy group, the alkoxy carbonyl group, the acyl group, or the acyloxy radical as a substituent, the letter alkyl group of branching, or the cycloalkyl radical of 3-20 carbon numbers. However, it may join together mutually and Ra and Rb may form an alicyclic monocycle. A hydrogen atom or an alkyl group is expressed as Rd. As Re, the shape of a straight chain of one - 20 carbon numbers which may have a halogen atom, the alkoxy group, the alkoxy carbonyl group, the acyl group, or the acyloxy radical as a substituent, the letter alkyl group of branching, or the cycloalkyl radical of 3-20 carbon numbers is expressed.

[Claim 3] The positive type photoresist constituent according to claim 1 or 2 characterized by containing the repeat structural unit the above-mentioned (A) resin is further indicated to be by the following general formula (III).

[Formula 5]



Inside of a formula (III): Z2 expresses -O- or -N(R3)-. R3 expresses a hydrogen atom, a hydroxyl group, or -OSO2-R4 here. R4 expresses an alkyl group, a halo alkyl group, a cycloalkyl radical, or camphor residue.

[Claim 4] Furthermore, the positive type photoresist constituent according to claim 1 to 3 characterized by containing (D) organic base nature compound and (E) fluorine system, and/or a silicon system surface active agent.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the positive-resist constituent used for super-micro lithography processes, such as a VLSI and manufacture of a high capacity microchip, or other

photofabrication processes. Furthermore, in detail, generating of a development defect is mitigated and it is related with the positive type photoresist constituent with which prevention of generating of particle and mitigation of the sensibility fluctuation by the passage of time were attained.

[0002]

[Description of the Prior Art] in recent years, the integrated circuit is raising the degree of integration increasingly, and consists of the line breadth below a half micron in manufacture of semi-conductor substrates, such as a VLSI, -- processing of a detailed pattern has overly come to be needed. In order to fulfill the need, operating wavelength of the aligner used for photolithography is short-wave-ized increasingly, and by the time using the excimer laser light (XeCl, KrF, ArF, etc.) of short wavelength also in far ultraviolet rays is now examined, it will become. A chemistry multiplier system resist is one of those are used for the pattern formation of the lithography in this wavelength field.

[0003] Generally a chemistry multiplier system resist can be divided roughly into three kinds, the common-name two-component system, a 2.5 component system, and 3 component system. The two-component system has combined the compound (it is henceforth called the photo-oxide generating agent) and binder resin which generate an acid by the photolysis. This binder resin is resin which has in intramolecular the radical (it is also called an acidolysis nature machine) to which an operation of an acid decomposes into and the solubility in the inside of the alkali developer of resin is made to increase. A 2.5 component system contains the low molecular weight compound which has an acidolysis nature machine further in such the two-component system. 3 component system contains a photo-oxide generating agent, alkali fusibility resin, and the above-mentioned low molecular weight compound.

[0004] Although the above-mentioned chemistry multiplier system resist is suitable for ultraviolet rays or the photoresist for an far-ultraviolet-rays exposure, it is necessary to correspond to the demand characteristics on use further in it. The photoresist constituent which combined acrylic resin with still less (meta) absorption as a photoresist constituent for the ArF light sources than the styrene resin which carried out hydroxy ** partially with the compound which therefore generates an acid in light is proposed. For example, there are JP,7-199467,A, 7-252324, etc. By JP,6-289615,A, the resin the 3rd class carbon organic radical carried out [resin] the ester bond to the oxygen of the carboxyl group of an acrylic acid is indicated especially.

[0005] Although the acidolysis nature resin which repeats acrylic ester and fumaric-acid ester and is made into a structural unit is furthermore indicated by JP,7-234511,A, a pattern profile, substrate adhesion, etc. are inadequate and the actual condition is that the satisfactory engine performance is not obtained.

[0006] Furthermore, the resin with which the alicyclic hydrocarbon part was introduced for the purpose of dry etching resistance grant is proposed again. In JP,9-73173,A, JP,9-90637,A, and JP,10-161313,A, the alkali fusibility radical protected with the structure containing an alicyclic radical and its alkali fusibility radical **** with an acid, and the resist ingredient using an acid sensitivity compound including the structural unit made to serve as alkali fusibility is indicated.

[0007] Moreover, the resist constituent which contains in JP,9-90637,A, 10-207069, and a 10-274852 official report the acidolysis nature resin which has specific lactone structure is indicated.

[0008] In order that the lithography process which manufactures the device using a design rule (0.18 micrometers and 0.13 micrometers or less) may use light with a wavelength of 193nm as exposure radiation

in many cases, it asks for the resist polymer which seldom contains ethylene system partial saturation nature. In JP,10-10739,A and JP,10-307401,A, although the transparency over the wavelength of 193nm improves, when it cannot necessarily be said to be high sensitivity but the lithography after 0.13 micrometer is considered, the resist engine performance in which resolving power is insufficient etc. is insufficient. The resist of the chemistry magnification mold containing the terpolymer which has the specific repeat structural unit which has norbornene structure in a principal chain is indicated by JP,10-130340,A. However, the problem of being as changing sensibility by preservation with the passage of time **** [, and] generated the resist of such a chemistry magnification mold. [that particle occurs at the time of still producing a defect at the time of development, or melting solid content to a solvent or the time of preservation with the passage of time]

[0009]

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is offering the positive type photoresist constituent with which generating of a development defect was mitigated in manufacture of a semiconductor device. Other purposes of this invention are offering the positive type photoresist constituent which can prevent generating of the particle at the time of melting solid content to a solvent, or the time of preservation with the passage of time, and can prevent fluctuation of the sensibility by preservation with the passage of time further.

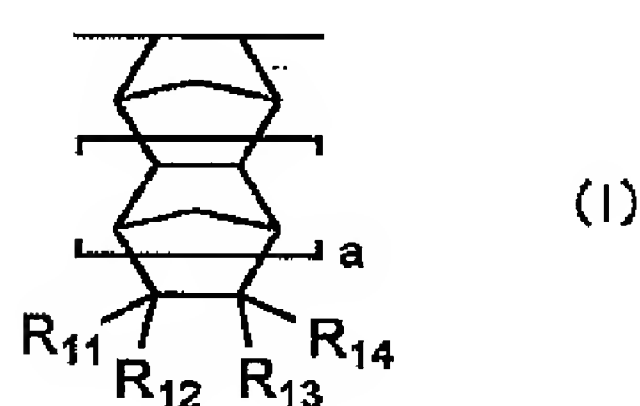
[0010]

[Means for Solving the Problem] As a result of examining wholeheartedly the component of a positive type chemistry multiplier system resist constituent, by using together the acidolysis nature resin which has the repeat structural unit of specific structure, and a specific solvent, this invention person etc. knew that the purpose of this invention would be attained, and resulted in this invention. That is, the above-mentioned purpose is attained by the following configuration.

[0011] (1) The repeat structural unit shown by the repeat structural unit shown by the (A) following general formula (I) and the following general formula (II) is contained. The partially aromatic solvent containing at least one sort chosen from the (Compound C) following solvent A group which generates an acid by the exposure of the resin which the dissolution rate to an alkali developer increases according to an operation of an acid, (B) activity beam of light, or a radiation, and at least one sort chosen from a following solvent B group, Or the partially aromatic solvent A group:chain-like ketone B group containing at least one sort chosen from a following solvent A group, and at least one sort chosen from a following solvent C group : Lactic-acid alkyl, Alkoxy alkyl propionate, acetic ester, and a propylene-glycol monoalkyl-ether C group: The positive type photoresist constituent characterized by containing gamma-butyrolactone, ethylene carbonate, and propylene carbonate.

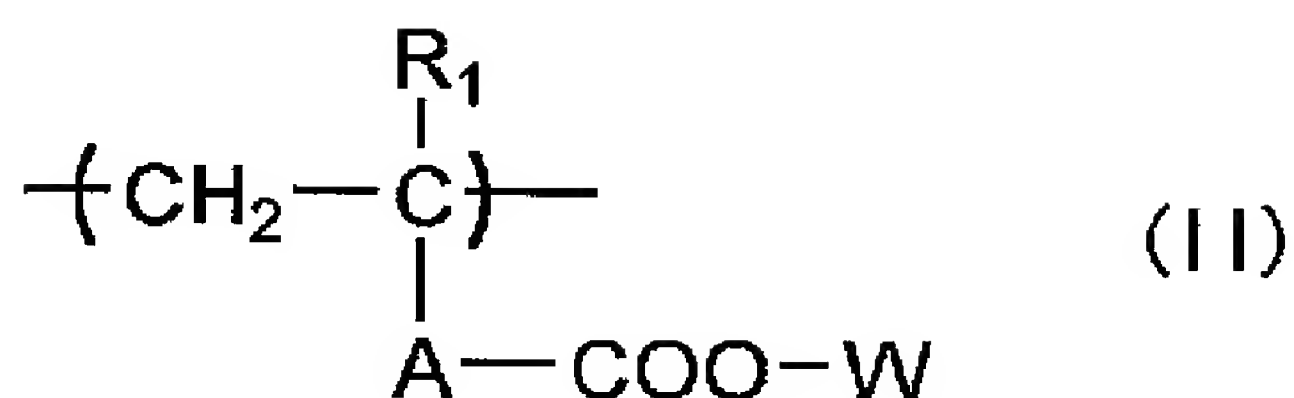
[0012]

[Formula 6]



[0013]

[Formula 7]



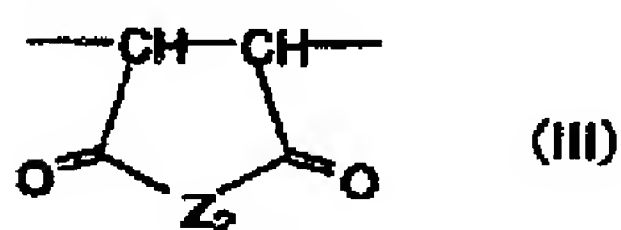
[0014] R11-R14 express respectively the alkyl group which may have a hydrogen atom or a substituent independently among a general formula (I). a is 0 or 1. R1 expresses a hydrogen atom or a methyl group among a general formula (II). A expresses the combination of independent [which is chosen from the group which consists of single bond, an alkylene group, a cyclo alkylene group, a ether group, a thioether radical, a carbonyl group, and an ester group], or two radicals or more. W expresses the radical expressed with the radical or -CH(Rd)-O-Re expressed with -C (Ra), (Rb), and (Rc). Here, Ra, Rb, and Rc express respectively the shape of a straight chain of one - 20 carbon numbers which may have a halogen atom, the alkoxy group, the alkoxy carbonyl group, the acyl group, or the acyloxy radical as a substituent, the letter alkyl group of branching, or the cycloalkyl radical of 3-20 carbon numbers. However, it may join together mutually and Ra and Rb may form an alicyclic monocycle. A hydrogen atom or an alkyl group is expressed as Rd. As Re, the shape of a straight chain of one - 20 carbon numbers which may have a halogen atom, the alkoxy group, the alkoxy carbonyl group, the acyl group, or the acyloxy radical as a substituent, the letter alkyl group of branching, or the cycloalkyl radical of 3-20 carbon numbers is expressed.

[0015] (2) The repeat structural unit shown by the repeat structural unit shown by the (A) above-mentioned general formula (I) and the above-mentioned general formula (II) is contained. The compound which generates an acid by the exposure of the resin which the dissolution rate to an alkali developer increases according to an operation of an acid, (B) activity beam of light, or a radiation, And the positive type photoresist constituent characterized by containing the partially aromatic solvent containing at least one sort chosen from a (C) above-mentioned solvent A group, at least one sort chosen from the above-mentioned solvent B group, and at least one sort chosen from the above-mentioned solvent C group.

[0016] (3) The above (1) characterized by containing the repeat structural unit the above-mentioned (A) resin is further indicated to be by the following general formula (III), or a positive type photoresist constituent given in (2).

[0017]

[Formula 8]



[0018] Inside of a formula (III): Z2 expresses -O- or -N(R3)-. R3 expresses a hydrogen atom, a hydroxyl group, or -OSO2-R4 here. R4 expresses an alkyl group, a halo alkyl group, a cycloalkyl radical, or camphor

residue.

(4) A positive type photoresist constituent given in either of above-mentioned (1) – (3) characterized by furthermore containing (D) organic base nature compound and a fluorine system, and/or a silicon system surface active agent.

[0019]

[Embodiment of the Invention] Hereafter, the component used for this invention is explained to a detail.

[1] Resin which the dissolution rate to an alkali developer increases according to an operation of the (A) acid (henceforth "acidolysis nature resin"). In the general formula (I) showing the repeat structural unit of acidolysis nature resin, R11–R14 express the alkyl group which may have a hydrogen atom or a substituent. As an alkyl group of R11–R14, the thing of carbon numbers 1–12 is desirable, is a thing of carbon numbers 1–10 more preferably, and can mention preferably a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, t-butyl, a pentyl radical, a hexyl group, a heptyl radical, an octyl radical, a nonyl radical, and a decyl group concretely. As a substituent of this alkyl group, a hydroxy group, an alkoxy group, an alkoxy alkoxy group, etc. are mentioned, and it is four or less carbon number preferably. a is 0 or 1 among a general formula (I).

[0020] R1 expresses a hydrogen atom or a methyl group among the general formula (II) showing the repeat structural unit of acidolysis nature resin. In a general formula (II), the radical expressed with the following type can be mentioned as an alkylene group of A.

– Rf and Rg express a hydrogen atom, an alkyl group, a permutation alkyl group, a halogen atom, a hydroxyl group, and an alkoxy group among the [C (Rf) and (Rg)] r-above-mentioned type, and even if both are the same, they may differ. As an alkyl group, low-grade alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, and butyl, are chosen from a methyl group, an ethyl group, a propyl group, and an isopropyl group desirable still more preferably. As a substituent of a permutation alkyl group, a hydroxyl group, a halogen atom, and an alkoxy group can be mentioned. As an alkoxy group, the thing of the carbon numbers 1–4, such as a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, can be mentioned. As a halogen atom, a chlorine atom, a bromine atom, a fluorine atom, iodine atom, etc. can be mentioned. r is the integer of 1–10. In a general formula (II), as a cyclo alkylene group of A, ten things are mentioned from a carbon number 3, and a cyclo pentene radical, a cyclo hexylene radical, a cyclo octylene radical, etc. can be mentioned.

[0021] W in a general formula (II) is a radical which constitutes the radical which becomes together with ester structure (–COO–) and is decomposed according to an operation of an acid, and expresses the radical expressed with the radical or –CH(Rd)–O–Re expressed with –C (Ra), (Rb), and (Rc). Here, Ra, Rb, and Rc express respectively the shape of a straight chain of one – 20 carbon numbers which may have a halogen atom, the alkoxy group, the alkoxy carbonyl group, the acyl group, or the acyloxy radical as a substituent, the letter alkyl group of branching, or the cycloalkyl radical of 3–20 carbon numbers. However, it may join together mutually and Ra and Rb may form an alicyclic monocycle. A hydrogen atom or an alkyl group is expressed as Rd. As Re, the shape of a straight chain of one – 20 carbon numbers which may have a halogen atom, the alkoxy group, the alkoxy carbonyl group, the acyl group, or the acyloxy radical as a substituent, the letter alkyl group of branching, or the cycloalkyl radical of 3–20 carbon numbers is expressed.

[0022] As the shape of a straight chain of one – 20 carbon numbers and the letter alkyl group of branching of

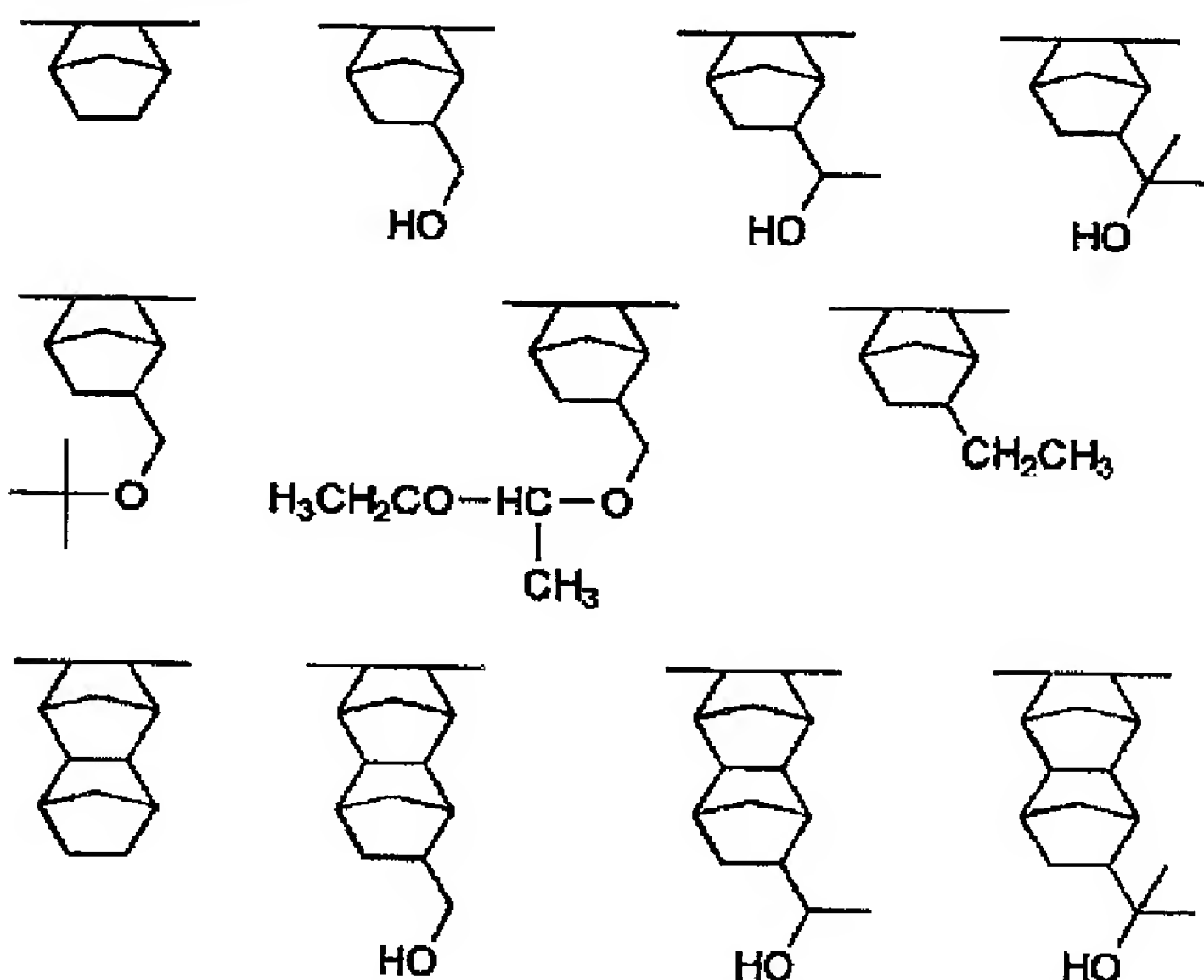
Ra, Rb, Rc, and Re, the thing of carbon numbers 1–12 is desirable, is a thing of carbon numbers 1–10 more preferably, and can mention preferably a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, t-butyl, a pentyl radical, a hexyl group, a heptyl radical, an octyl radical, a nonyl radical, and a decyl group concretely. As a cycloalkyl radical of 3–20 carbon numbers of Ra, Rb, Rc, and Re, a cyclopentyl group, a cyclohexyl radical, a cyclo octyl radical, etc. can be mentioned. As an alkyl group of Rd, the alkyl group of carbon numbers 1–4 is desirable, and can specifically mention a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, t-butyl, etc. A cyclopentane, a cyclohexane, cyclooctane, etc. can be mentioned as an alicyclic monocycle which Ra and Rb combine mutually and form.

[0023] In the further substituent of the shape of a straight chain of one – 20 carbon numbers of Ra, Rb, Rc, and Re, the letter alkyl group of branching, or the cycloalkyl radical of 3–20 carbon numbers, the thing of the carbon numbers 1–4, such as a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, can be mentioned as an alkoxy group in :alkoxy group and an alkoxy carbonyl group. As a halogen atom, a chlorine atom, a bromine atom, a fluorine atom, iodine atom, etc. can be mentioned. A formyl group, a ** NZOIRU radical, etc. are mentioned as an acyl group. Propyl carbonyloxy group, a benzoyloxy radical, etc. are mentioned as an acyloxy radical. 1-alkoxy ethyl groups, such as alkoxy methyl groups, such as the 3rd class alkyl groups, such as t-butyl, t-amyl group, a 2-cyclohexyl-2-propyl group, and 1-methylcyclohexyl radical, an ethoxy methyl group, and an ethoxy ethoxy methyl group, 1-ethoxyethyl radical, and 1-isopropoxy ethyl group, can be mentioned preferably as W of a general formula (II).

[0024] Although the example of the monomer which is equivalent to the repeat structural unit shown by the general formula (I) hereafter is shown, it is not limited to these.

[0025]

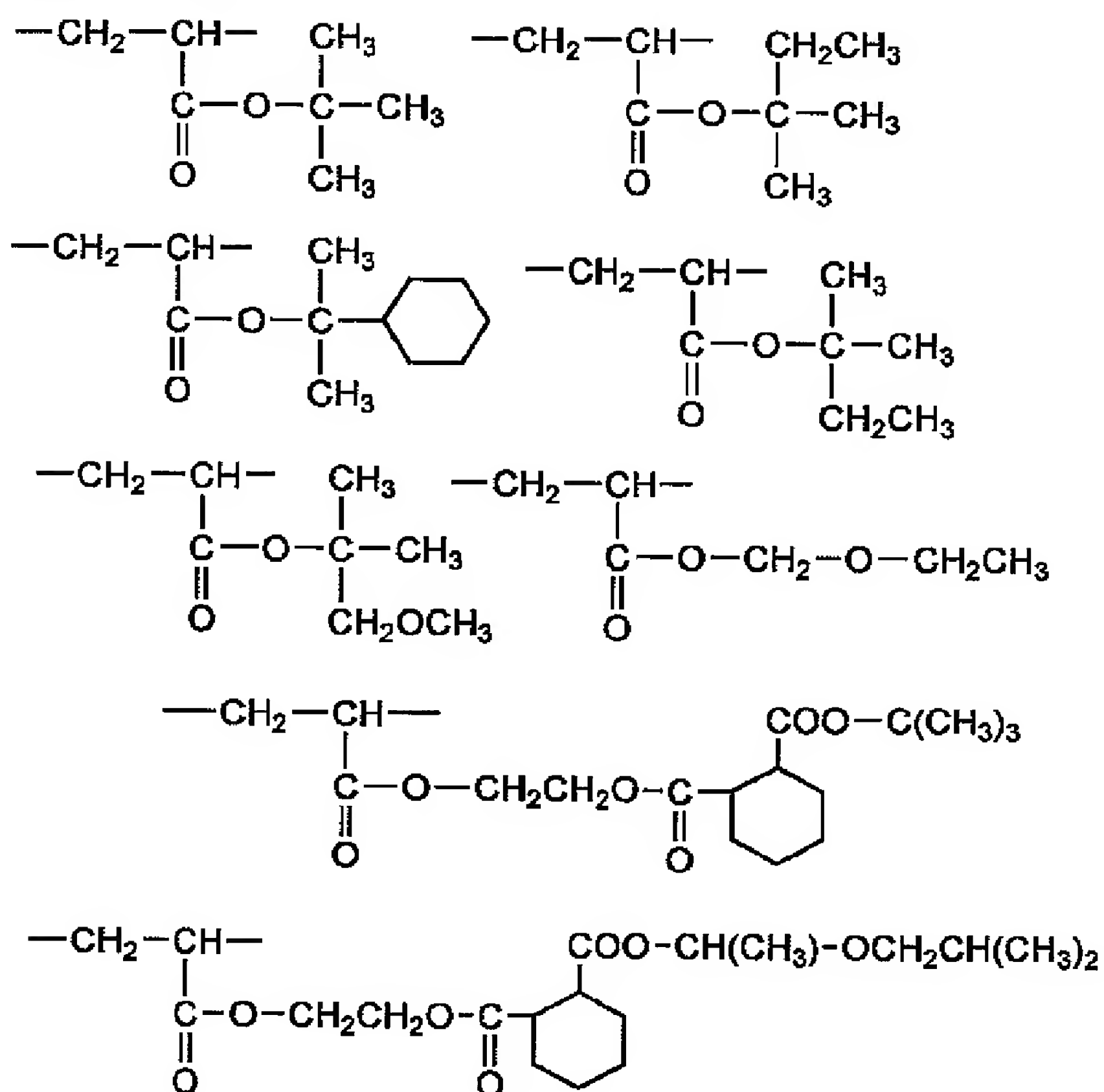
[Formula 9]



[0026] Although the example of the monomer which is equivalent to the repeat structural unit shown by the general formula (II) hereafter is shown, it is not limited to these.

[0027]

[Formula 10]



[0028] (b) acidolysis nature resin of this invention can contain the repeat unit further shown by the general formula (III).

[0029] In a general formula (III), Z2 expresses $-\text{O}-$ or $-\text{N}(\text{R}3)-$. R3 expresses a hydrogen atom, a hydroxyl group, or $-\text{O}-\text{SO}_2-\text{R}4$ here. R4 expresses an alkyl group, a halo alkyl group, a cycloalkyl radical, or camphor residue.

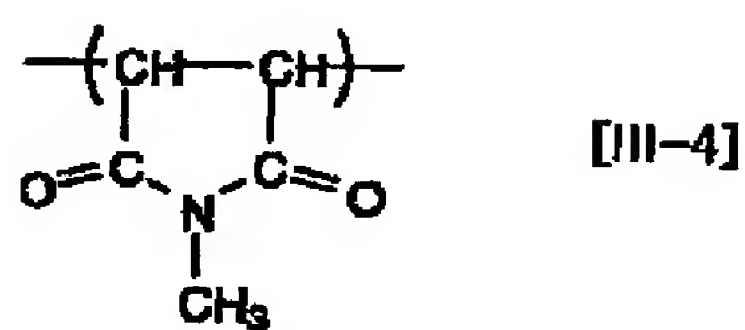
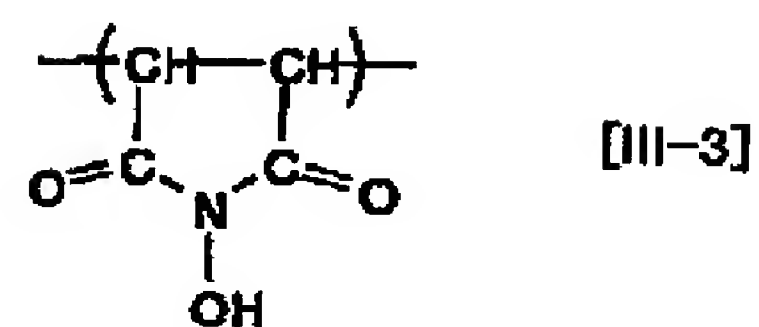
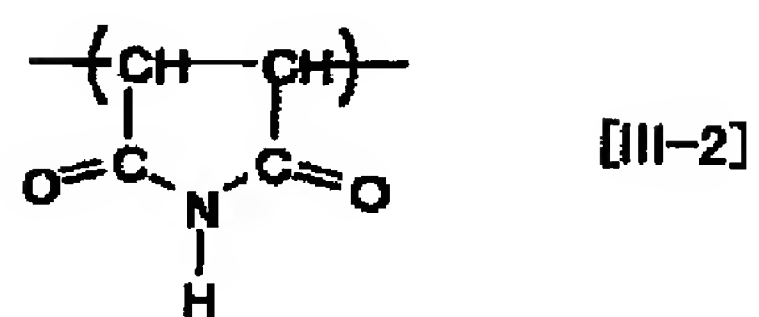
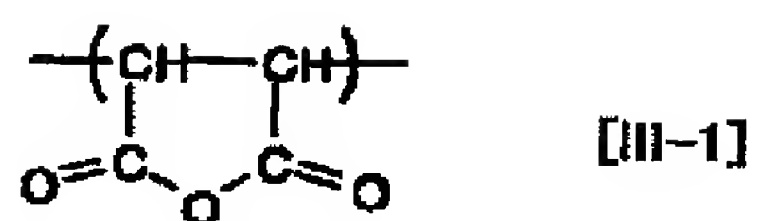
[0030] As an alkyl group in the above R4, the shape of a straight chain of 1-10 carbon numbers and the letter alkyl group of branching are desirable, are the shape of a straight chain of 1-6 carbon numbers, and a letter alkyl group of branching more preferably, and are a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, and t-butyl still more preferably.

[0031] Above R4 As a halo alkyl group which can be set, a trifluoromethyl radical, nano fluoro butyl, a PENTA deca fluoro octyl radical, a TORIKURORO methyl group, etc. can be mentioned. As a cycloalkyl radical in the above R4, a cyclopentyl group, a cyclohexyl radical, a cyclo octyl radical, etc. can be mentioned.

[0032] Although the example of the monomer which is equivalent to the repeat structural unit shown by the general formula (III) hereafter is shown, it is not limited to these.

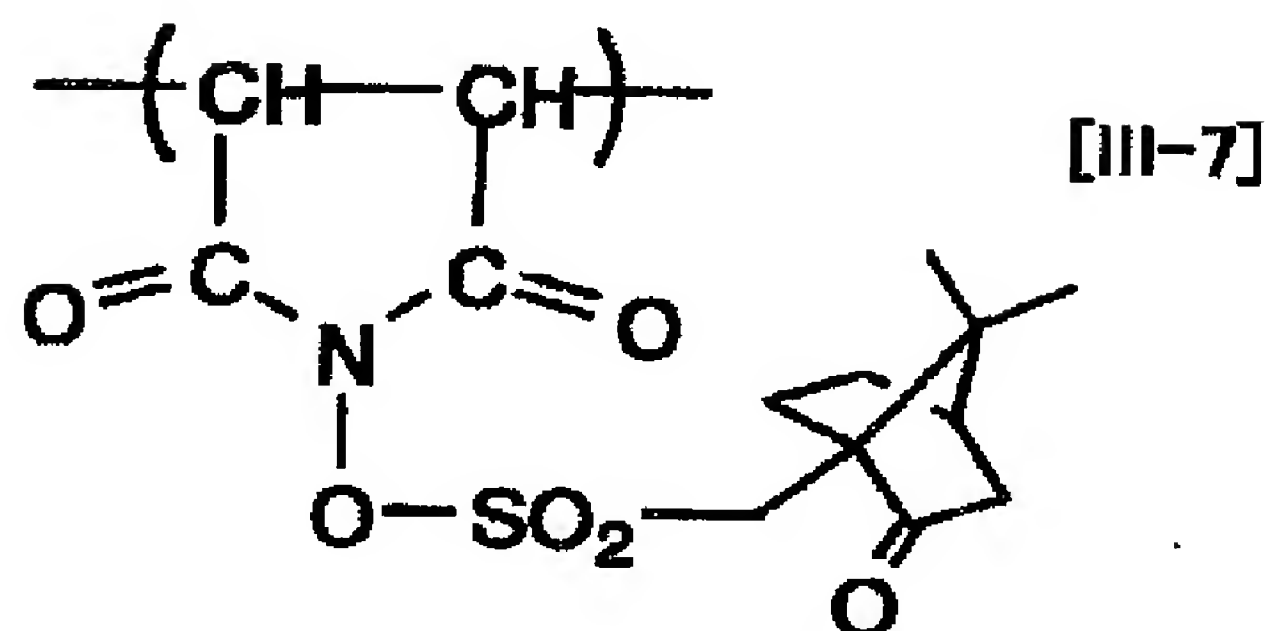
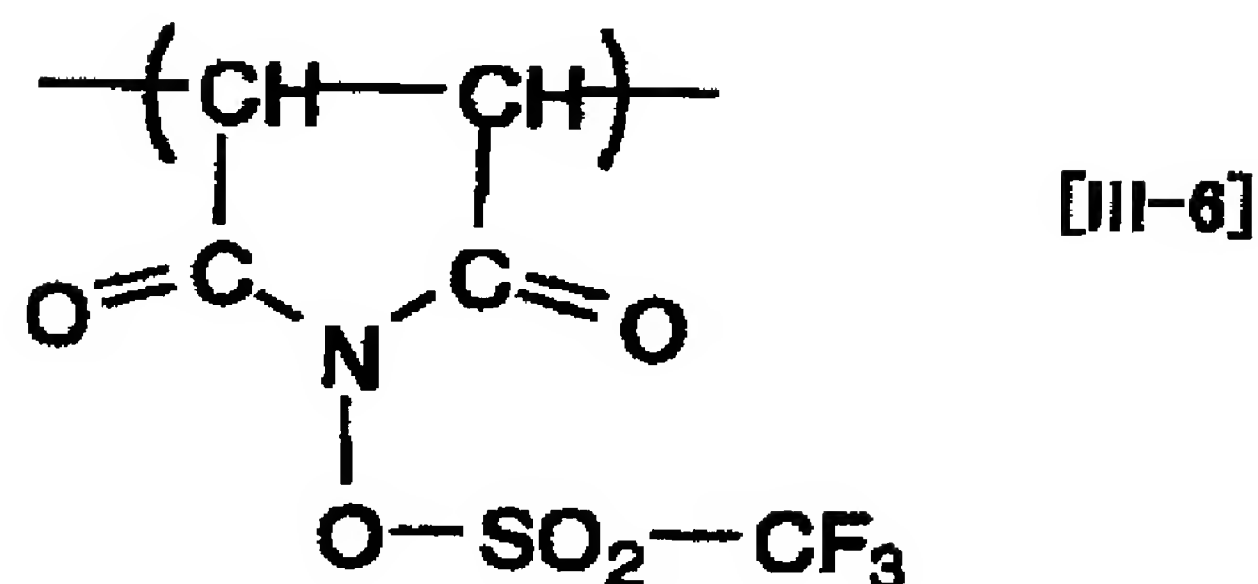
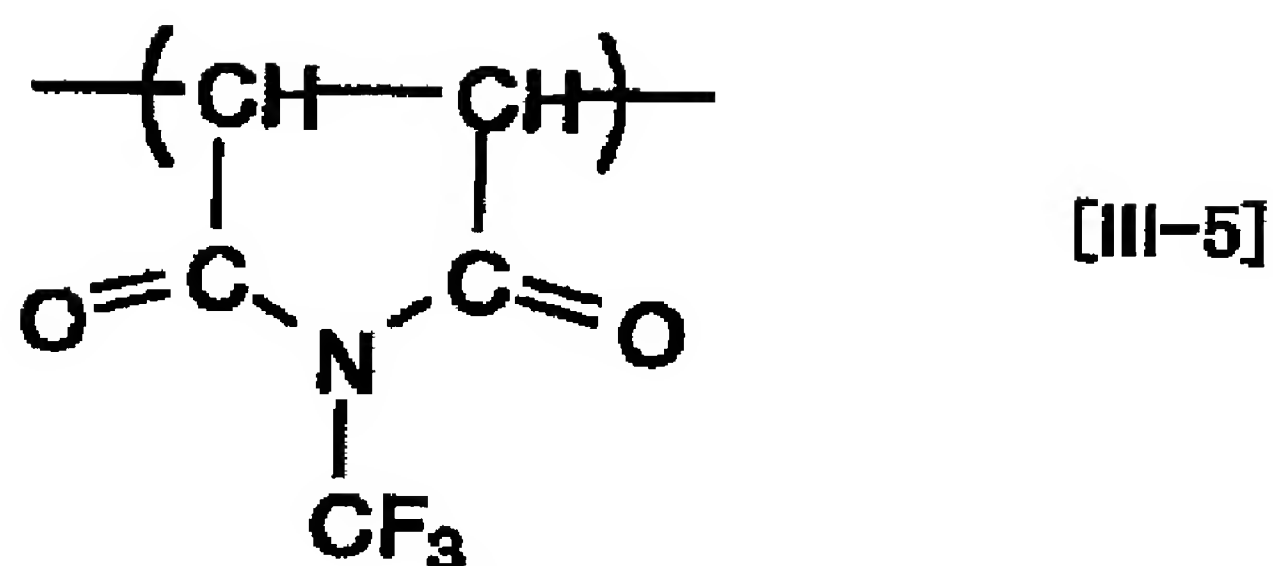
[0033]

[Formula 11]



[0034]

[Formula 12]



[0035] (A) In addition to the above-mentioned repeat structural unit, further, the acidolysis nature resin which is a component can contain various repeat structural units in order to adjust dry etching resistance, standard developer fitness and substrate adhesion, a resist profile, the resolution that is the general required property of a resist, thermal resistance, sensibility, etc.

[0036] Although the repeat structural unit equivalent to the following monomer can be mentioned as such a repeat structural unit, it is not limited to these. Thereby, fine tuning of the adhesion to the substrate of the engine performance required of acidolysis nature resin, the solubility over (1) spreading solvent, (2) film-production nature (glass transition point), (3) alkali development property, (4) ***** (relative-degree-of-intimacy aquosity, alkali fusibility radical selection), and (5) unexposed parts, (6) dry-etching resistance, etc. is attained especially.

[0037] The compound which has one addition polymerization nature unsaturated bond chosen from for example, acrylic ester, methacrylic ester, acrylamides, methacrylamide, an allyl compound, vinyl ether, and vinyl ester as such a monomer can be mentioned.

[0038] Specifically, the following monomers can be mentioned. Acrylic ester (the carbon number of an alkyl group is alkyl acrylate of 1-10 preferably): A methyl acrylate, An ethyl acrylate, acrylic-acid propyl,

acrylic-acid amyl, acrylic-acid cyclohexyl, Acrylic-acid ethylhexyl, acrylic-acid octyl, acrylic-acid-t-octyl, Chlorethyl acrylate, 2-hydroxyethyl acrylate 2, 2-dimethyl hydroxypropyl acrylate, 5-hydroxy pentyl acrylate, trimethylol propane monoacrylate, pentaerythritol monoacrylate, benzyl acrylate, methoxybenzyl acrylate, furfuryl acrylate, tetrahydrofurfuryl acrylate, etc.

[0039] Methacrylic ester (the carbon number of an alkyl group is alkylmetaacrylate of 1-10 preferably) : Methyl methacrylate, Ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, Amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, Benzyl methacrylate, KURORU benzyl methacrylate, octyl methacrylate, 2-hydroxyethyl methacrylate, 4-hydroxy butyl methacrylate, 5-hydroxy pentyl methacrylate, 2, and 2-dimethyl-3-hydroxypropyl methacrylate, Trimethylol propane mono-methacrylate, pentaerythritol mono-methacrylate, furfuryl methacrylate, tetrahydrofurfuryl methacrylate, etc.

[0040] Acrylamides: Acrylamide, N-alkyl acrylamide (carbon numbers 1-10 as an alkyl group) for example, there are a methyl group, an ethyl group, a propyl group, butyl, t-butyl, a heptyl radical, an octyl radical, a cyclohexyl radical, a hydroxyethyl radical, etc. N and N-dialkyl acrylamide (carbon numbers 1-10 as an alkyl group) For example, N-hydroxyethyl-N-methylacrylamide, N-2-acetamidoethyl-N-acetyl acrylamide, etc. with a methyl group, an ethyl group, butyl, an isobutyl radical, an ethylhexyl radical, a cyclohexyl radical, etc.

[0041] Methacrylamide: Methacrylamide, N-alkyl methacrylamide (as alkyl group, there are thing of carbon numbers 1-10, for example, methyl group, ethyl group, t-butyl, ethylhexyl radical, hydroxyethyl radical, cyclohexyl radical, etc.), N, and N-dialkyl methacrylamide (there are an ethyl group, a propyl group, butyl, etc. as an alkyl group), N-hydroxyethyl-N-methyl methacrylamide, etc.

[0042] Allyl compound: Allyl ester, allyloxy ethanol (for example, an acetic-acid allyl compound, allyl caproate, a caprylic-acid allyl compound, a lauric-acid allyl compound, a palmitic-acid allyl compound, a stearin acid allyl compound, allyl benzoate, an acetoacetic-acid allyl compound, a lactic-acid allyl compound, etc.), etc.

[0043] vinyl ether: -- alkyl vinyl ether (for example, hexyl vinyl ether --) Octyl vinyl ether, DESHIRU vinyl ether, ethylhexyl vinyl ether, Methoxy ethyl vinyl ether, ethoxyethyl vinyl ether, KURORU ethyl vinyl ether, The 1-methyl -2, 2-dimethyl propyl vinyl ether, 2-ethyl butyl vinyl ether, Hydroxyethyl vinyl ether, diethylene-glycol vinyl ether, dimethylaminoethyl vinyl ether, diethylamino ethyl vinyl ether, butylamino ethyl vinyl ether, benzyl vinyl ether, tetrahydrofurfuryl vinyl ether, etc.

[0044] Vinyl ester: Vinyl butyrate, vinyl iso butyrate, vinyl trimethyl acetate, vinyl diethyl acetate, vinyl BARETO, vinyl caproate, vinyl KURORU acetate, vinyl dichloro acetate, vinyl methoxy acetate, vinyl butoxy acetate, vinyl acetoacetate, vinyl lactate, vinyl-beta-phenyl butyrate, vinyl cyclohexyl carboxylate, etc.

[0045] Itaconic-acid dialkyls: Dimethyl itaconate, itaconic-acid diethyl, dibutyl itaconate, etc. The dialkyl ester or monoalkyl ester of boletic acid; dibutylfumarate etc.

[0046] In addition, a crotonic acid, an itaconic acid, acrylonitrile, a methacrylonitrile, MAREIRO nitril, etc.

[0047] In addition, copolymerization may be carried out as long as it is the unsaturated compound of the monomer equivalent to the above-mentioned various repeat structural units, and copolymerizable addition polymerization nature.

[0048] In acidolysis nature resin, further, the content mole ratio of each repeat structural unit is suitably set up, in order to adjust the dry etching resistance of a resist, standard developer fitness and substrate adhesion, a resist profile, the resolution that is the general requirement of a resist, thermal resistance, sensibility, etc.

[0049] the content of the repeat structural unit shown by the general formula in acidolysis nature resin (I) -- all inside of repeat structural unit, 25 - 70-mol % -- desirable -- more -- desirable -- 28 - 65-mol % -- it is 30 - 60-mol % still more preferably. moreover, the content of the repeat structural unit shown by the general formula (II) among acidolysis nature resin -- all inside of repeat structural unit, 2 - 50-mol % -- desirable -- more -- desirable -- 4 - 45-mol % -- it is 6 - 40-mol % still more preferably. the content of the repeat structural unit shown by the general formula (III) among acidolysis nature resin -- all 20-80-mol % in a repeat structural unit -- desirable -- more -- desirable -- 25-70-mol % -- it is 30-60-mol % still more preferably.

[0050] Moreover, although the content in the resin of the repeat structural unit based on other copolymerization components other than a general formula (I), (II), or (III) the repeat structural unit shown can also be suitably set up according to the engine performance of a desired resist Less than [99 mol %] is desirable to the total number of mols which generally totaled the repeat structural unit shown by the general formula (I) and (II), and it is less than [80 mol %] preferably [it is more desirable and] to a 90 mol % less or equal and a pan. In addition, when the constituent of this invention is an object for ArF exposure, as for the point of transparency over ArF light to acidolysis nature resin, it is desirable that an aromatic series ring is not included.

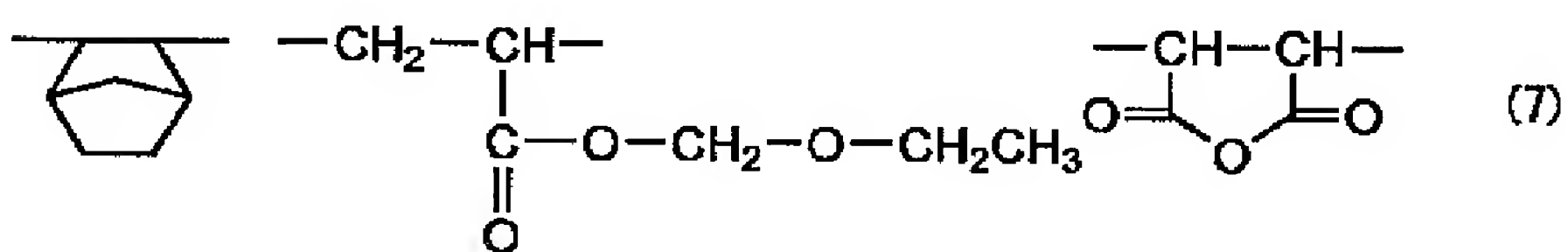
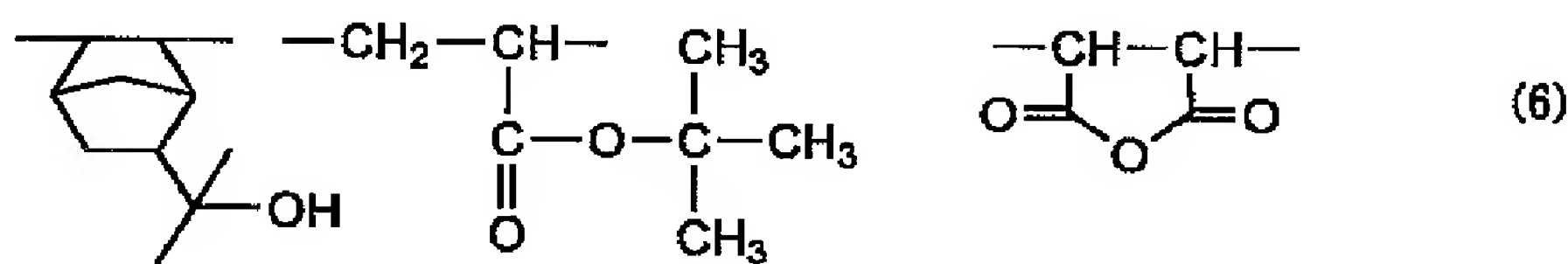
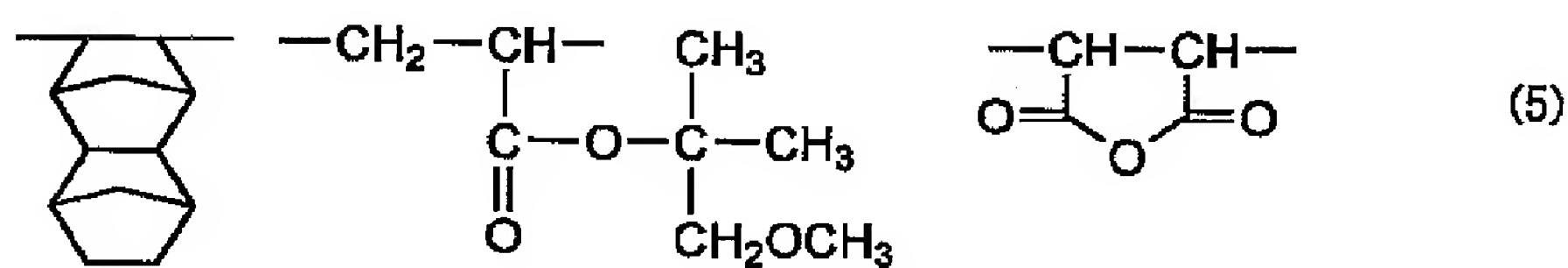
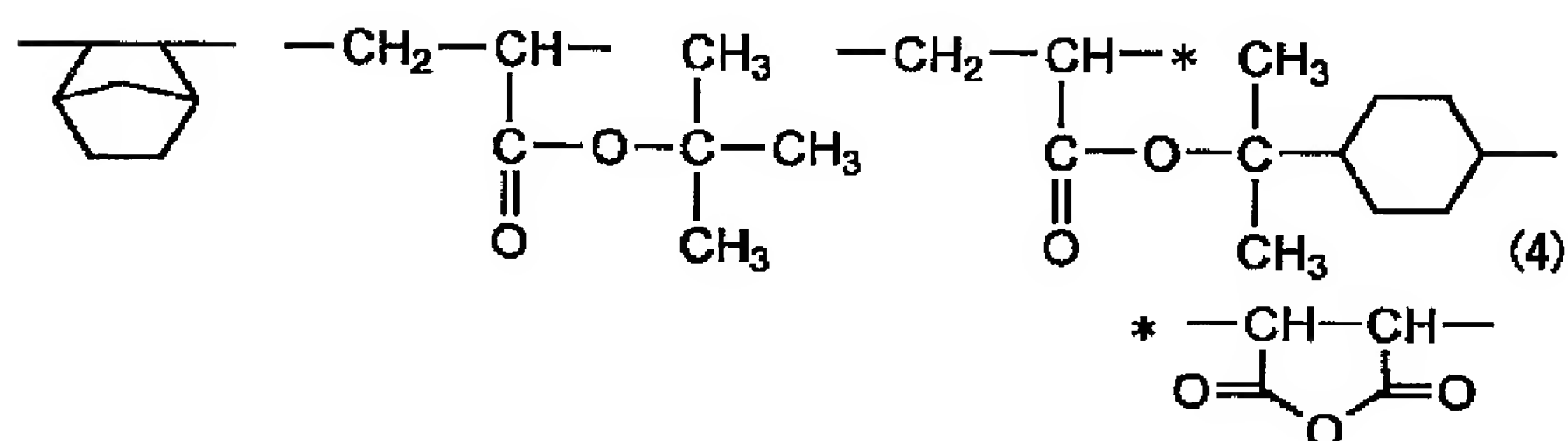
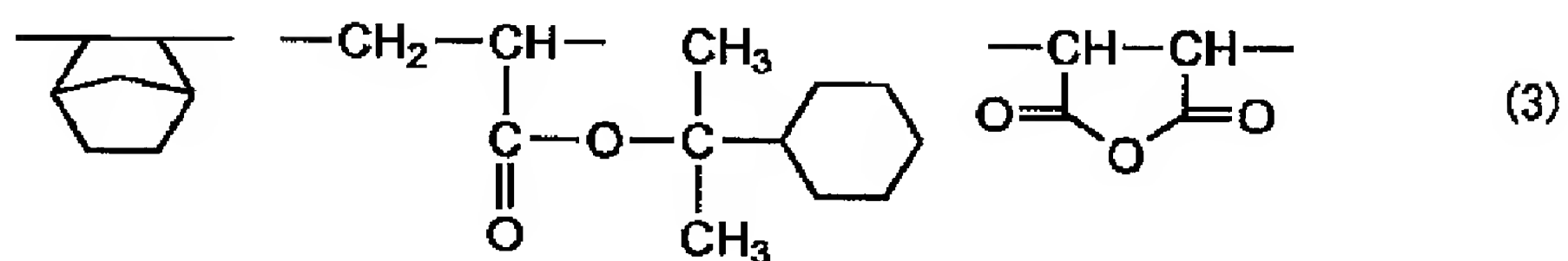
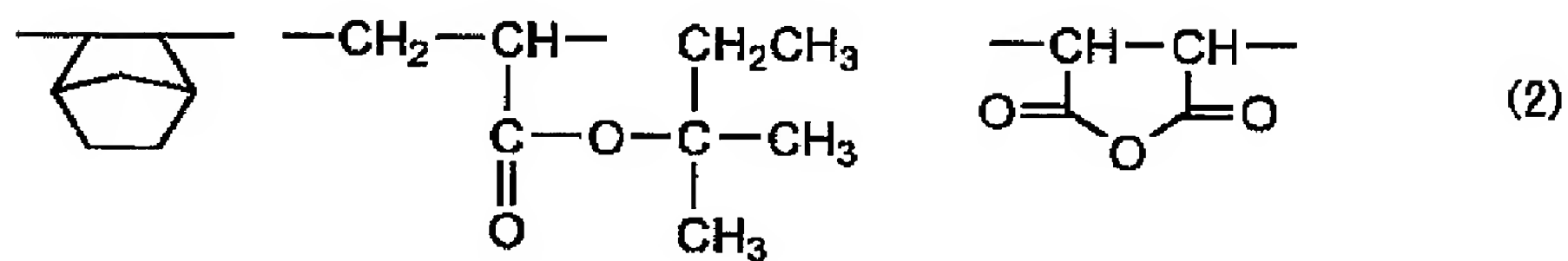
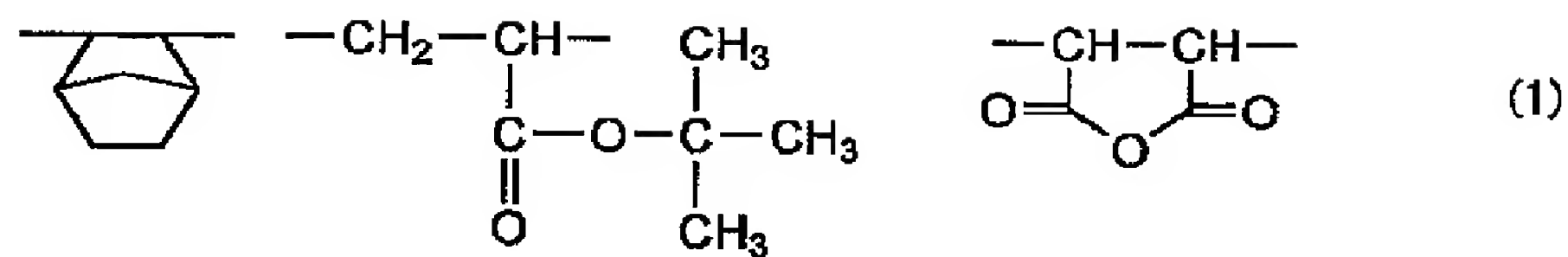
[0051] the molecular weight of the above acidolysis nature resin -- a weighted mean (polystyrene reduced property by the Mw:GPC method) -- it is -- desirable -- 1,000-1,000,000 -- more -- desirable -- 1,500-500,000 -- further -- desirable -- 2,000-200,000 -- it is the range of 2,500-100,000 still more preferably, and while thermal resistance etc. improves so that it is large, development nature etc. falls and it is adjusted to the desirable range by these balance. The acidolysis nature resin used for this invention is compoundable according to a conventional method (for example, radical polymerization).

[0052] In the positive type photoresist constituent of this invention, among total solids, the loadings in the whole resist constituent of acidolysis nature resin have 40 - 99.99 desirable % of the weight, and are 50 - 99.97 % of the weight more preferably.

[0053] Below, the example in which the combination of the repeat structural unit of the acidolysis nature resin which is the (A) component is desirable is shown.

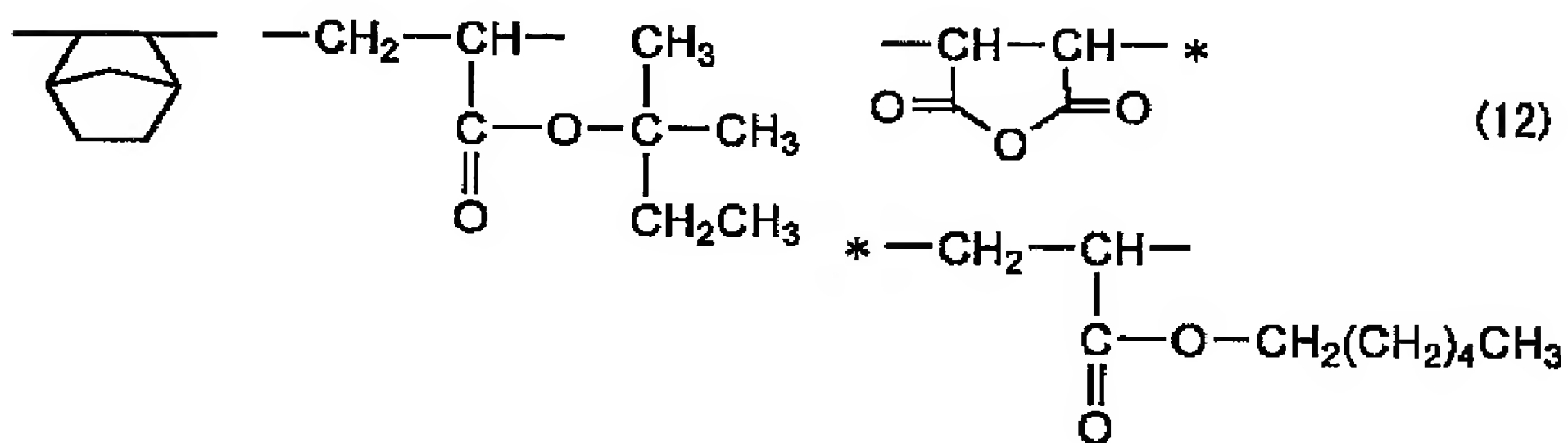
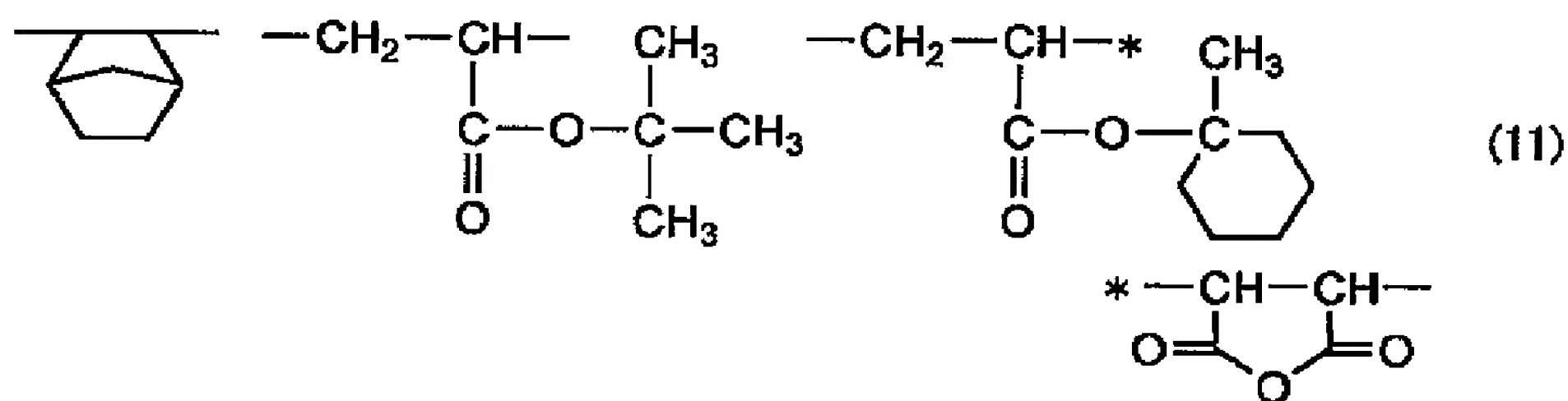
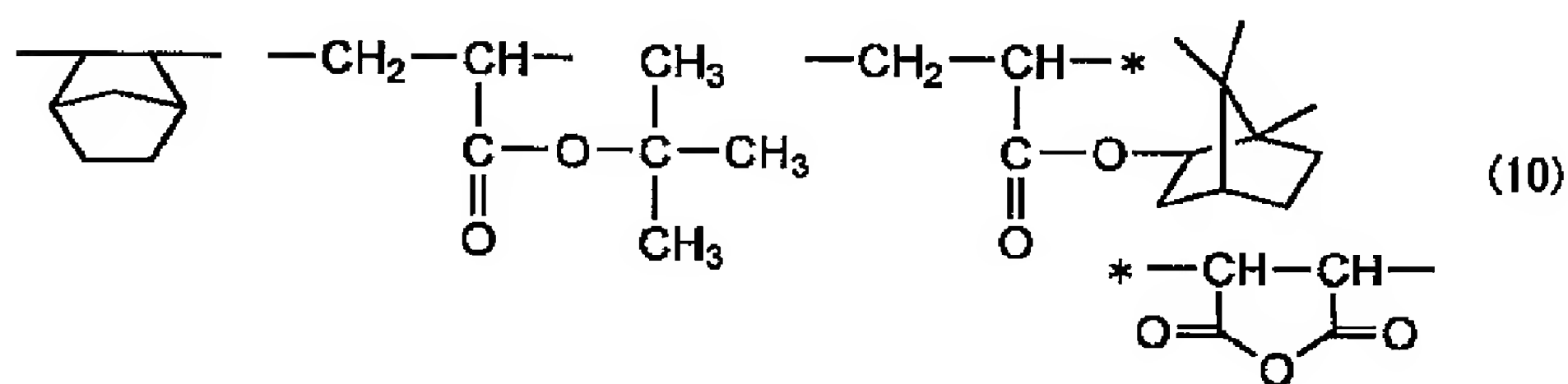
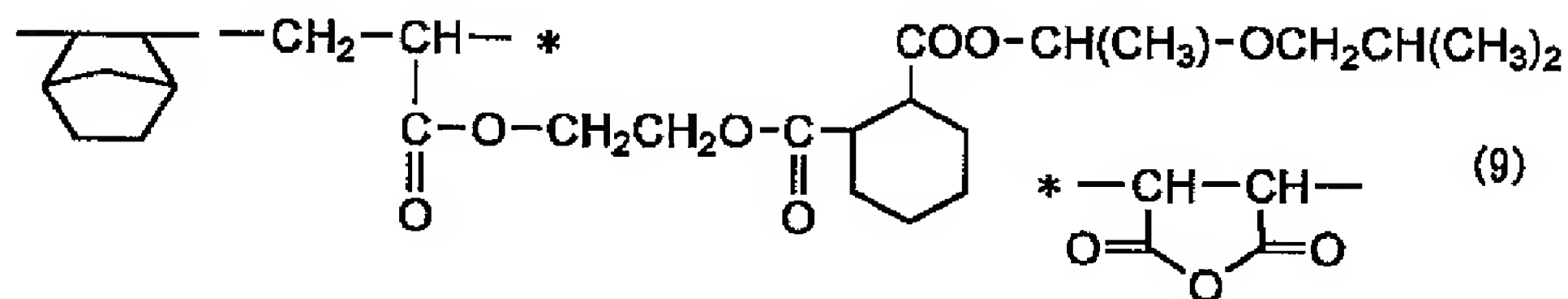
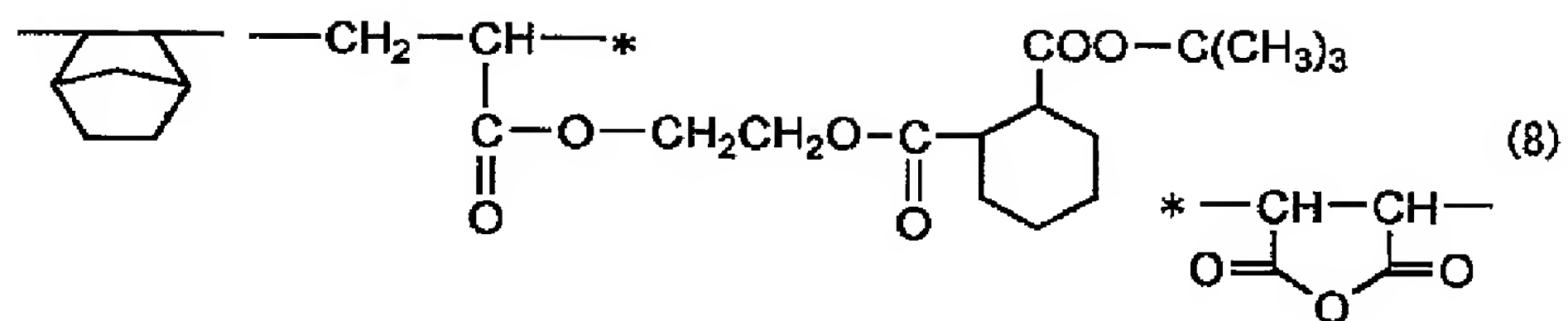
[0054]

[Formula 13]



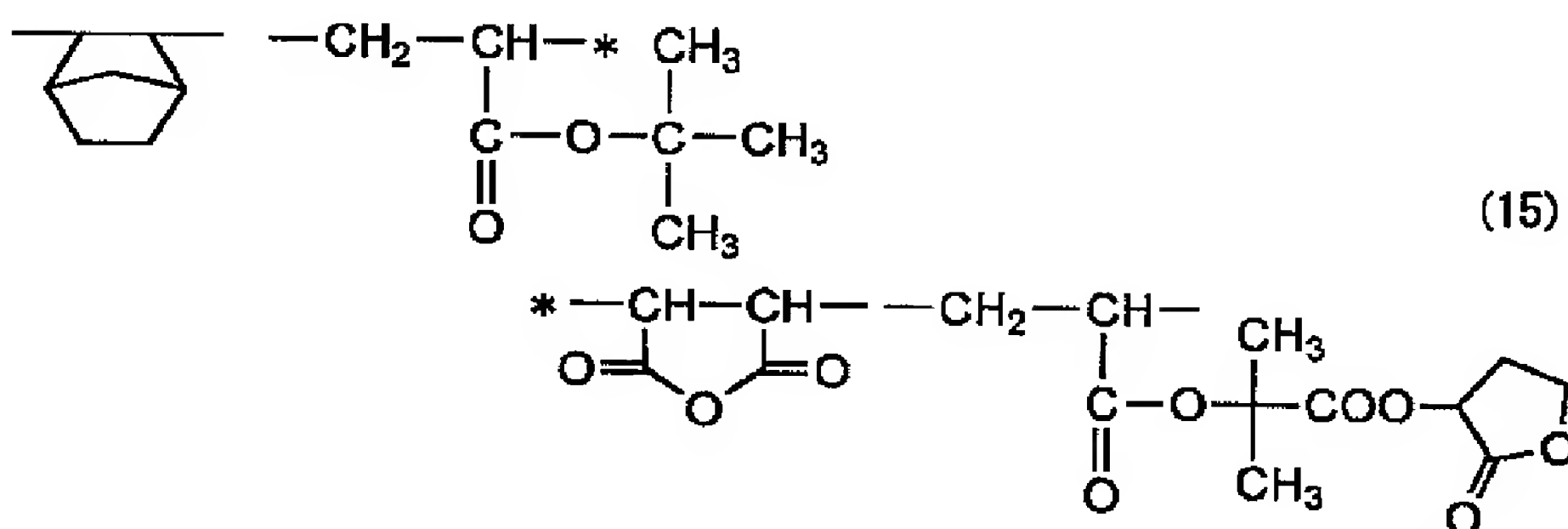
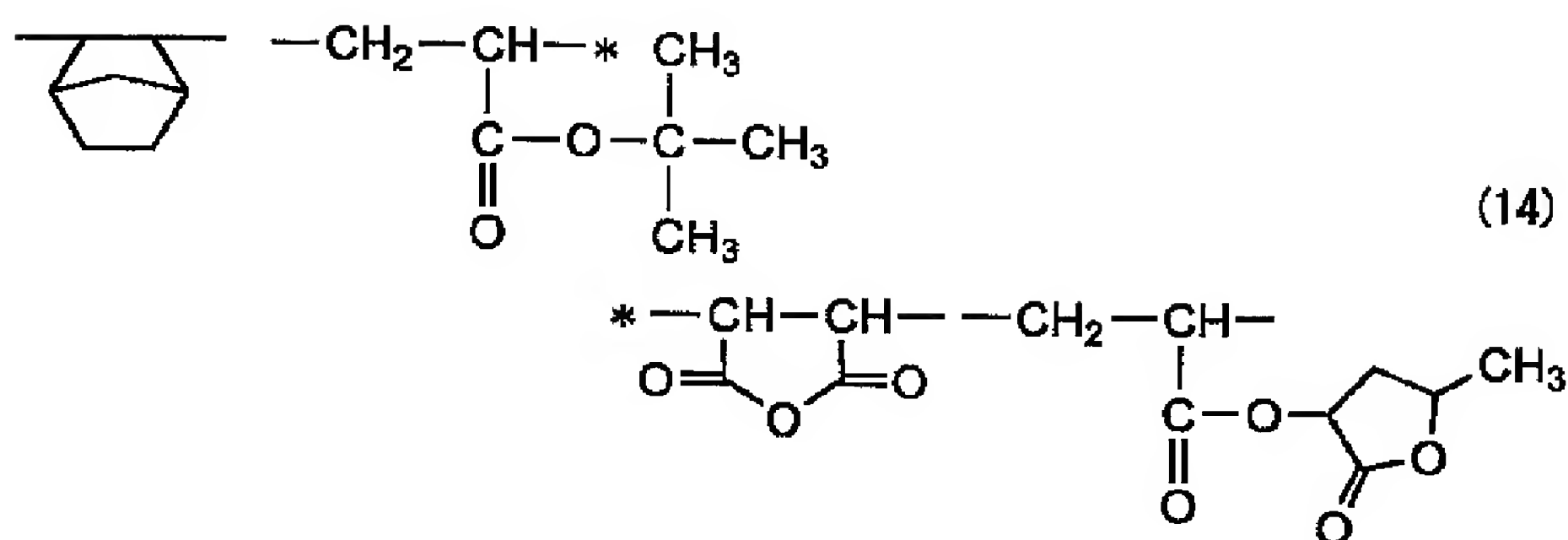
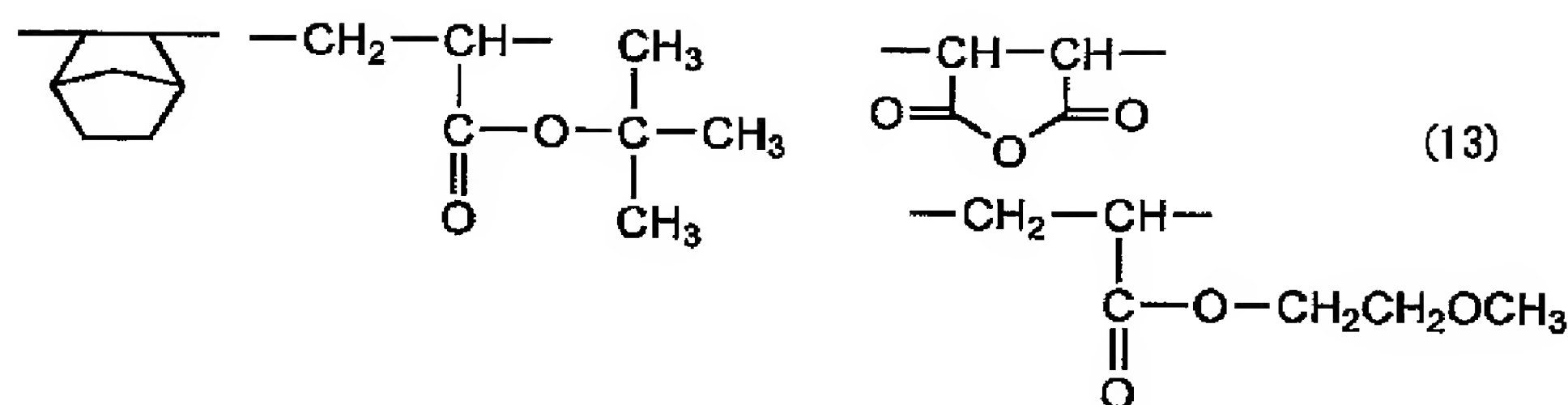
[0055]

[Formula 14]



[0056]

[Formula 15]



[0057] [2] Compound which generates an acid by the exposure of (B) activity beam of light or a radiation (photo-oxide generating agent)

The photo-oxide generating agent used by this invention is a compound which generates an acid by the exposure of an activity beam of light or a radiation. As a photo-oxide generating agent used by this invention, the photoinitiator of optical cationic polymerization, a well-known light (400–200nm ultraviolet rays and far ultraviolet rays — preferably especially) currently used for the photoinitiator of an optical radical polymerization, the optical decolorizing agent of coloring matter, optical alterant, or a micro resist The compounds which generate an acid by g line, h line, i line, KrF excimer laser light, ArF excimer laser light, the electron ray, the X-ray, the molecular beam, or the ion beam, and those mixture can be used choosing them suitably.

[0058] Moreover, the compound which is represented by onium salt, such as diazonium salt, ammonium salt, phosphonium salt, iodonium salt, sulfonium salt, a seleno NIUMU salt, and arsonium salt, an organic halogenated compound, an organic metal / organic halogenide, the photo-oxide generating agent that has o-nitrobenzyl mold protective group, imino sulfonate, etc. as a photo-oxide generating agent used for other this inventions, for example and which photodissociates and generates a sulfonic acid, a disulfon compound, a diazo keto sulfone, a diazo disulfon compound, etc. can be mentioned. Moreover, the radical which generates an acid by such light, or the compound which introduced the compound into the principal chain or side chain of a polymer can be used.

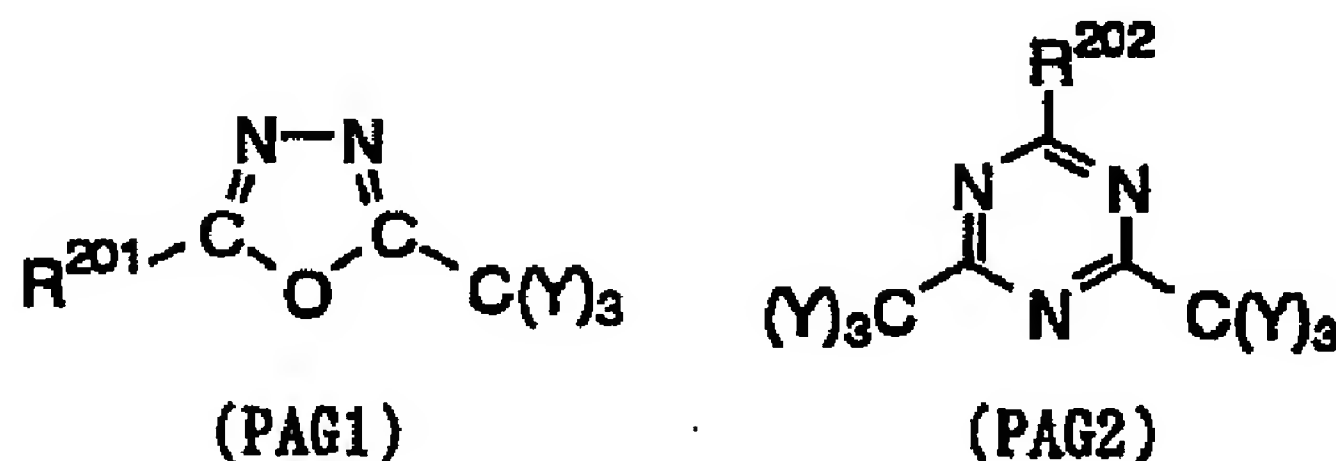
[0059] Furthermore, the compound which generates an acid by the light of a publication can also be used for V.N.R.Pillai, Synthesis, (1), 1 (1980), A.Abad et al, Tetrahedron Lett., (47) 4555 (1971), D.H.R.Barton et al, J.Chem.Soc., (C), 329 (1970), U.S. Pat. No. 3,779,778, the Europe patent No. 126,712, etc.

[0060] In the compound which decomposes by the exposure of the above-mentioned electron ray, and generates an acid, especially the thing used effectively is explained below.

(1) S-triazine derivative expressed with the oxazole derivative or general formula (PAG2) expressed with the following general formula (PAG1) which the trihalomethyl group permuted.

[0061]

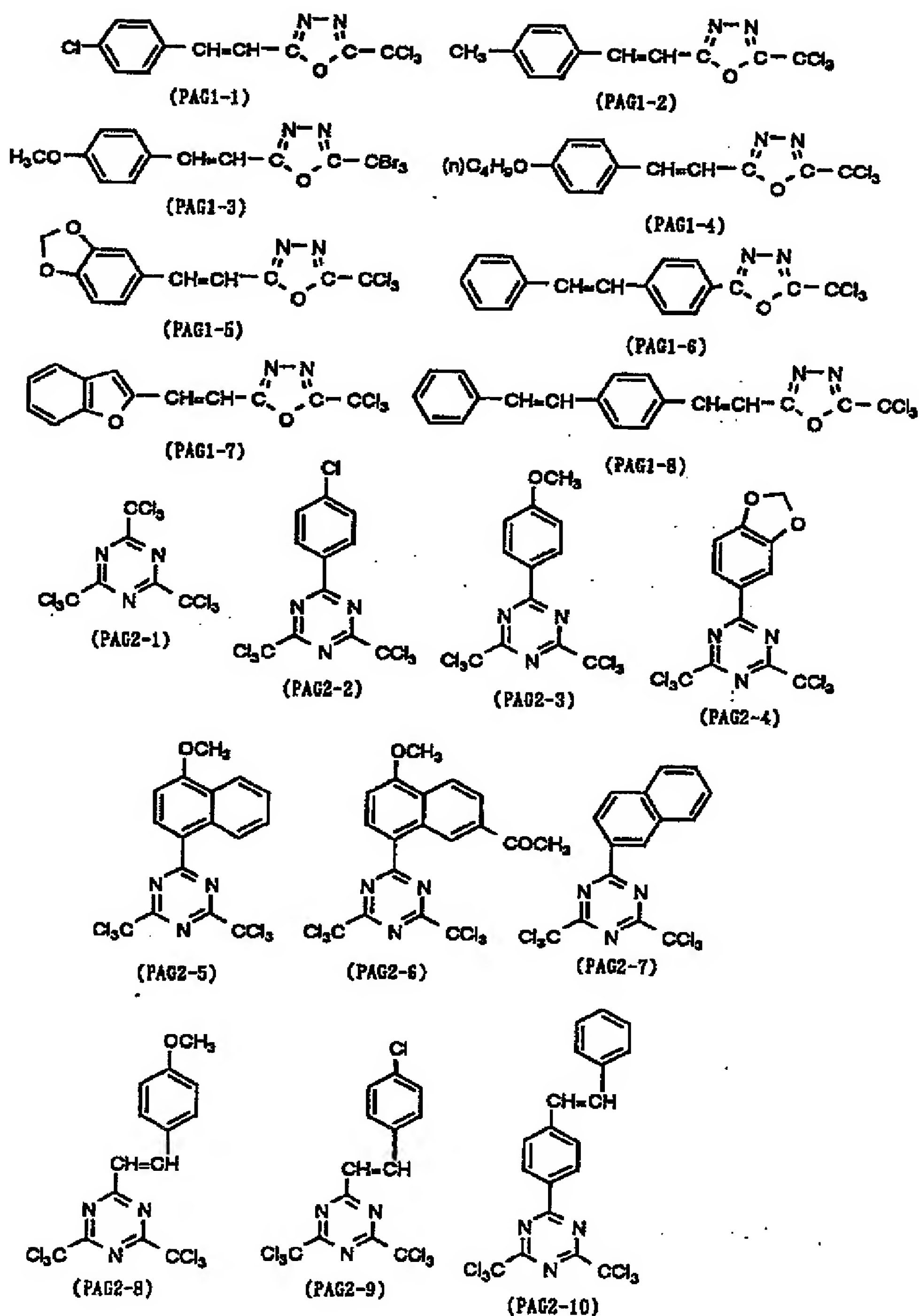
[Formula 16]



[0062] R201 shows among a formula the aryl group which is not permuted [a permutation or] and an alkenyl radical, and R202 shows the aryl group which is not permuted [a permutation or], an alkenyl radical, an alkyl group, and -C (Y)3. Y shows a chlorine atom or a bromine atom. Although the following compounds can specifically be mentioned, it is not limited to these.

[0063]

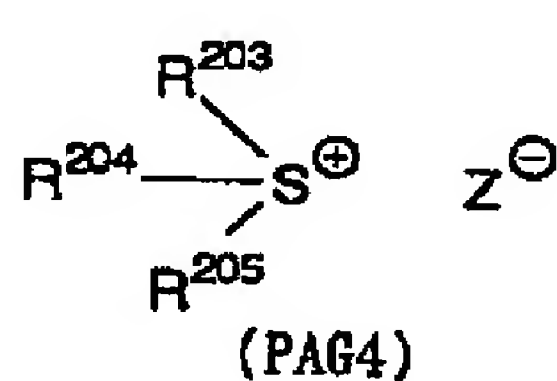
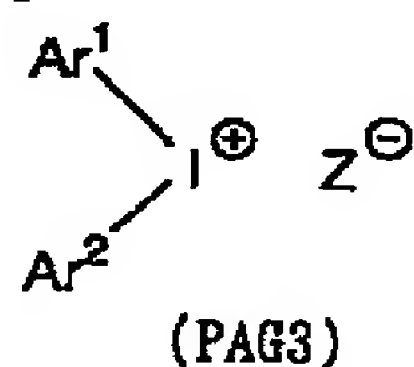
[Formula 17]



[0064] (2) Iodonium salt expressed with the following general formula (PAG3), or sulfonium salt expressed with a general formula (PAG4).

[0065]

[Formula 18]



[0066] Formulas Ar1 and Ar 2 show respectively the aryl group which is not permuted [a permutation or] independently here. R203, R204, and R205 show respectively the alkyl group which is not permuted [a permutation or] and an aryl group independently.

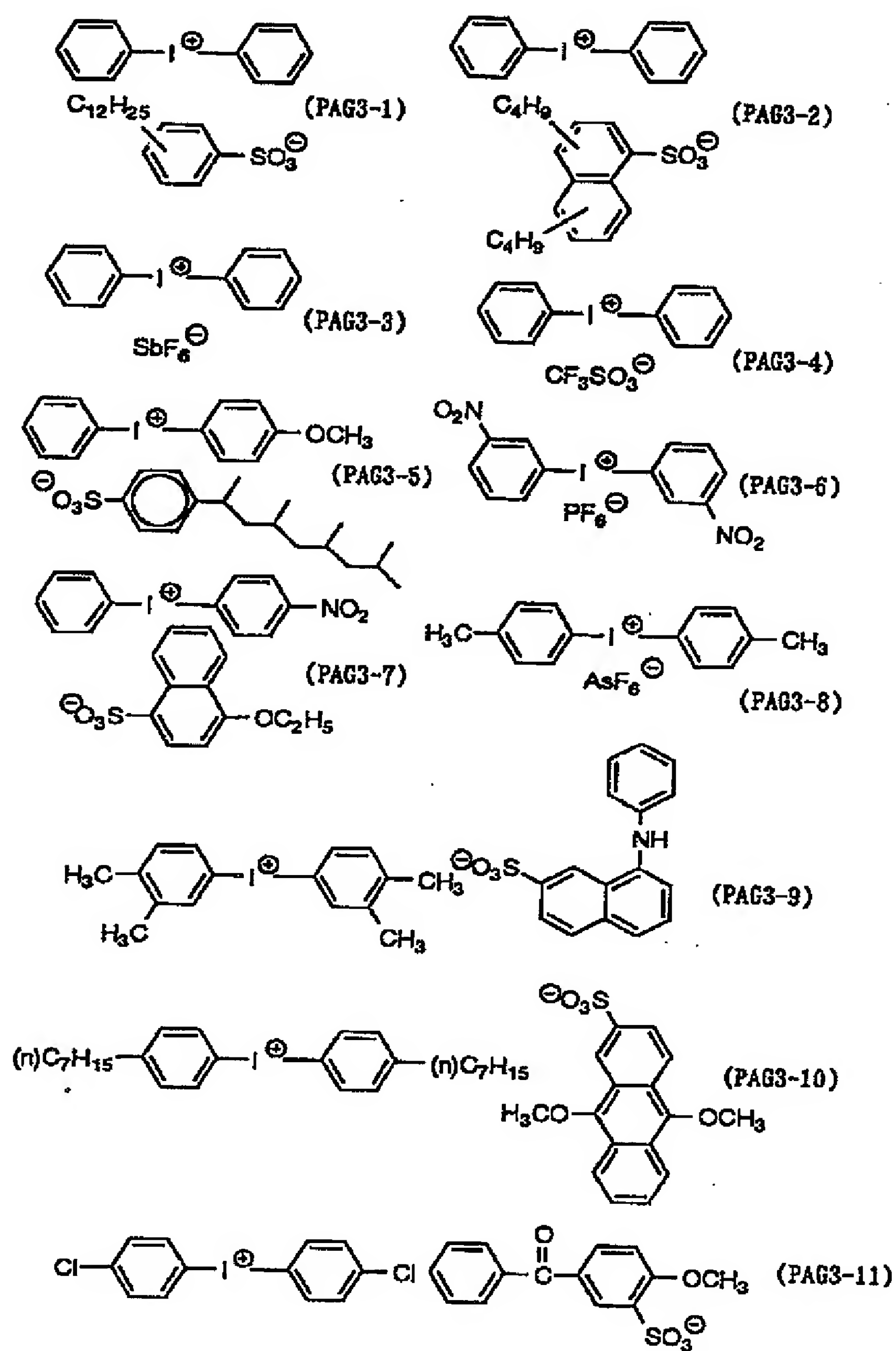
[0067] Z- shows an opposite anion, for example, is condensation polykaryotic aromatic series sulfonic-acid anions, such as perfluoro alkane sulfonic-acid anions, such as BF_4^- , AsF_6^- , PF_6^- , SbF_6^- , SiF_6^{2-} , ClO_4^- , and CF_3SO_3^- , a pentafluoro benzenesulfonic acid anion, and a naphthalene-1-sulfonic-acid anion, and an anthraquinone sulfonic acid. Although an anion, a sulfonic group content color, etc. can be mentioned, it is not limited to these.

[0068] Moreover, two, and Ar1 and Ar2 of R203, R204, and R205 may be combined through each single bond or substituent.

[0069] Although the compound shown below as an example is mentioned, it is not limited to these.

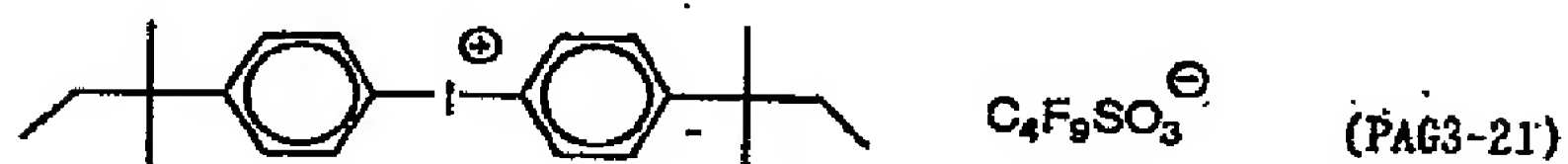
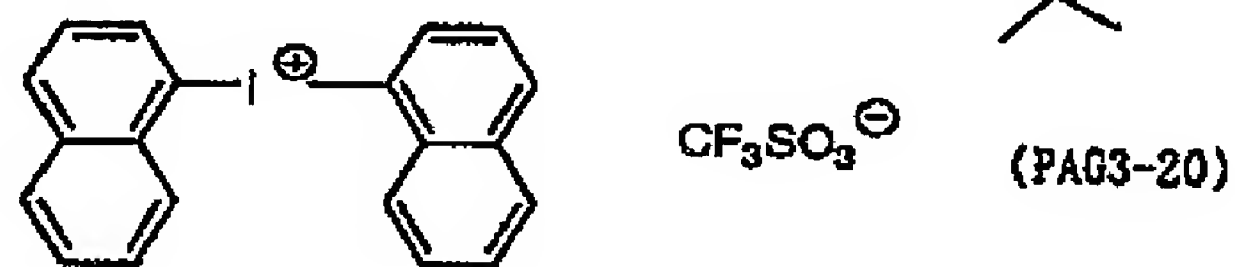
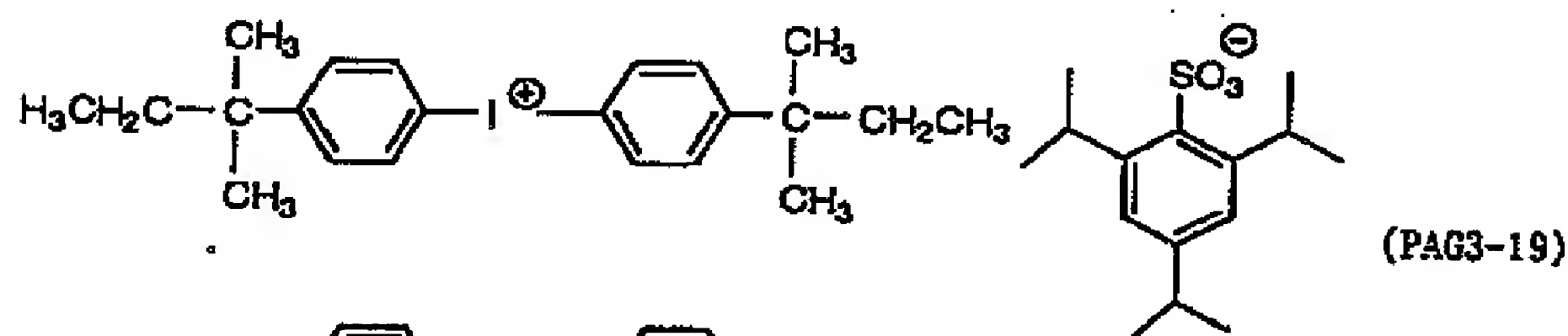
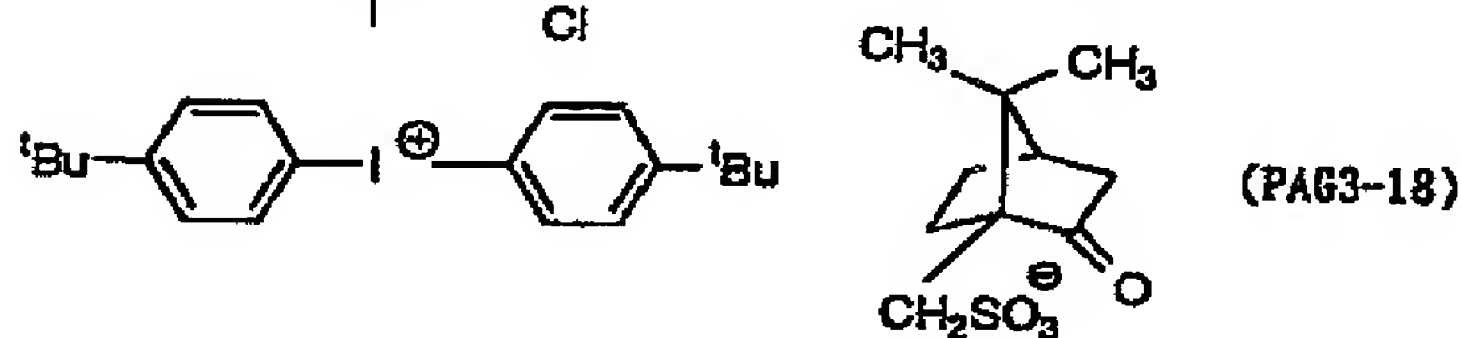
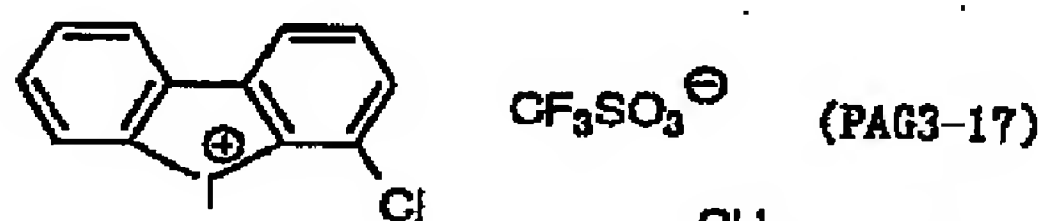
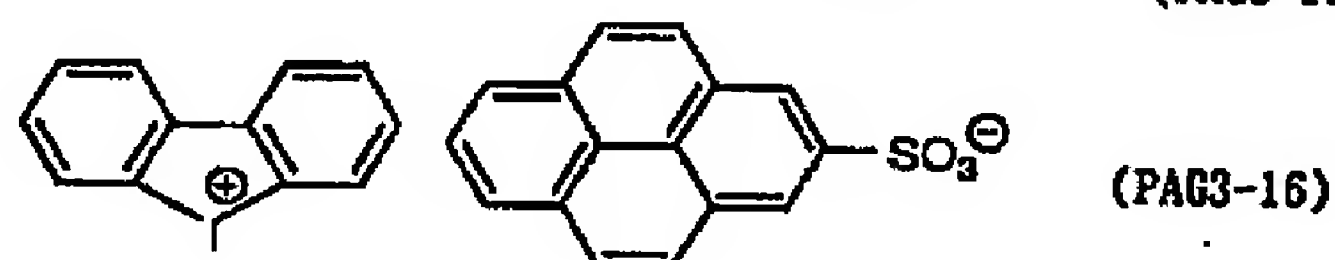
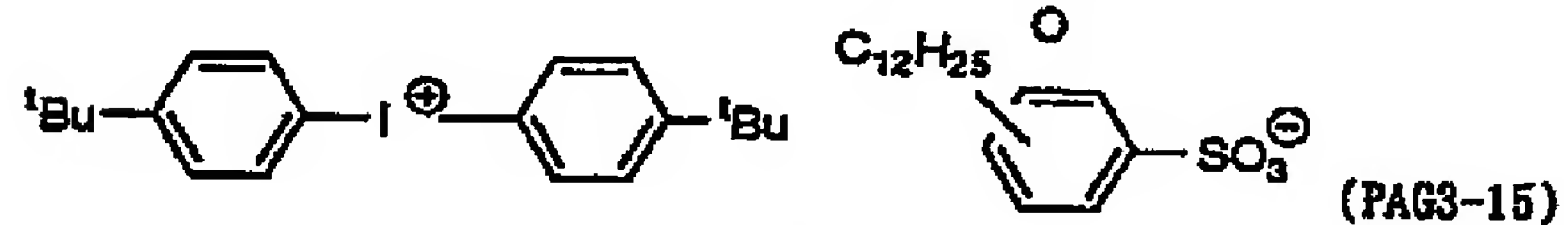
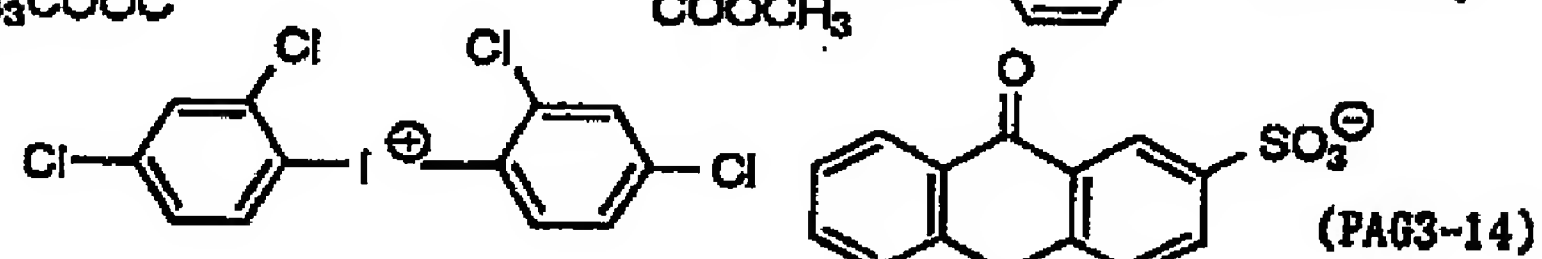
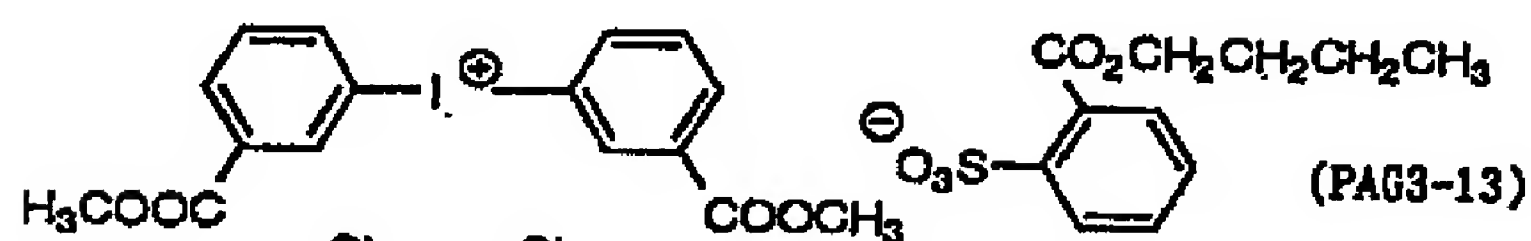
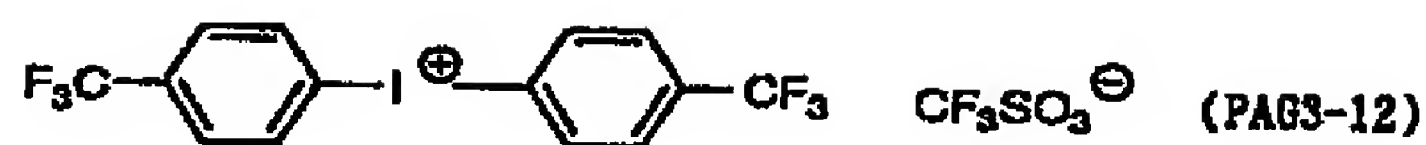
[0070]

[Formula 19]



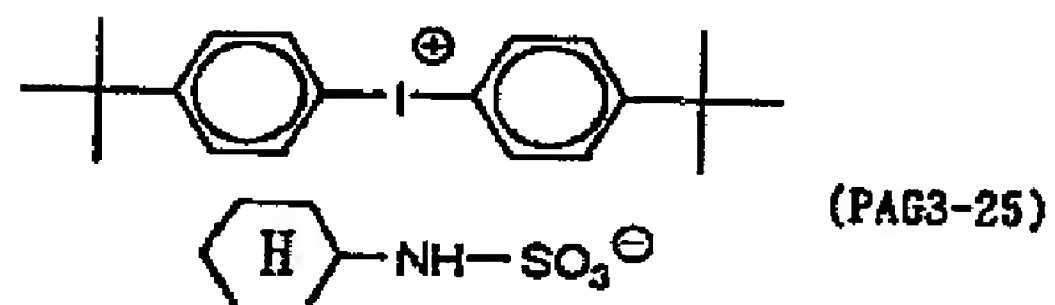
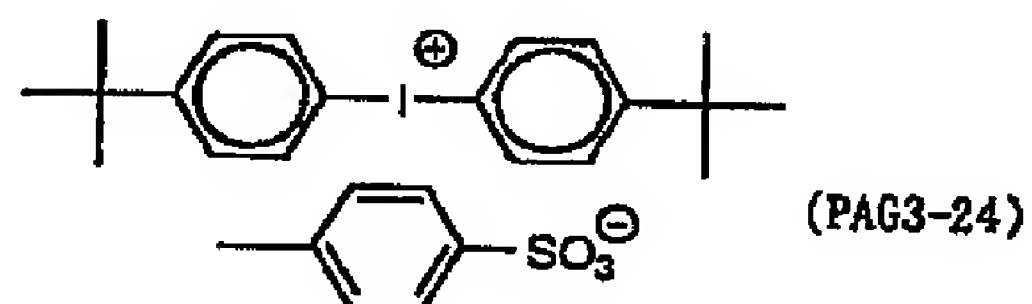
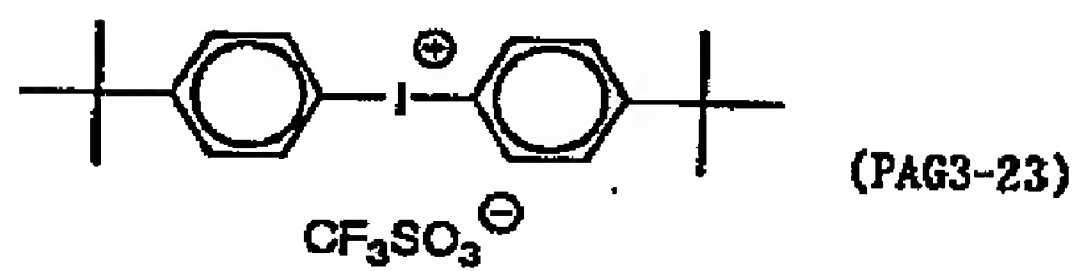
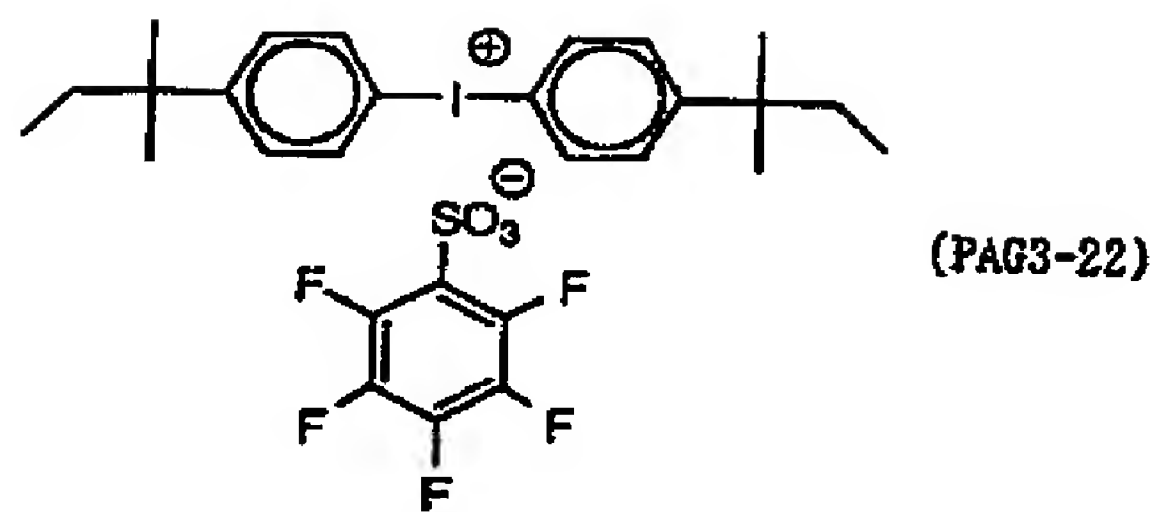
[0071]

[Formula 20]



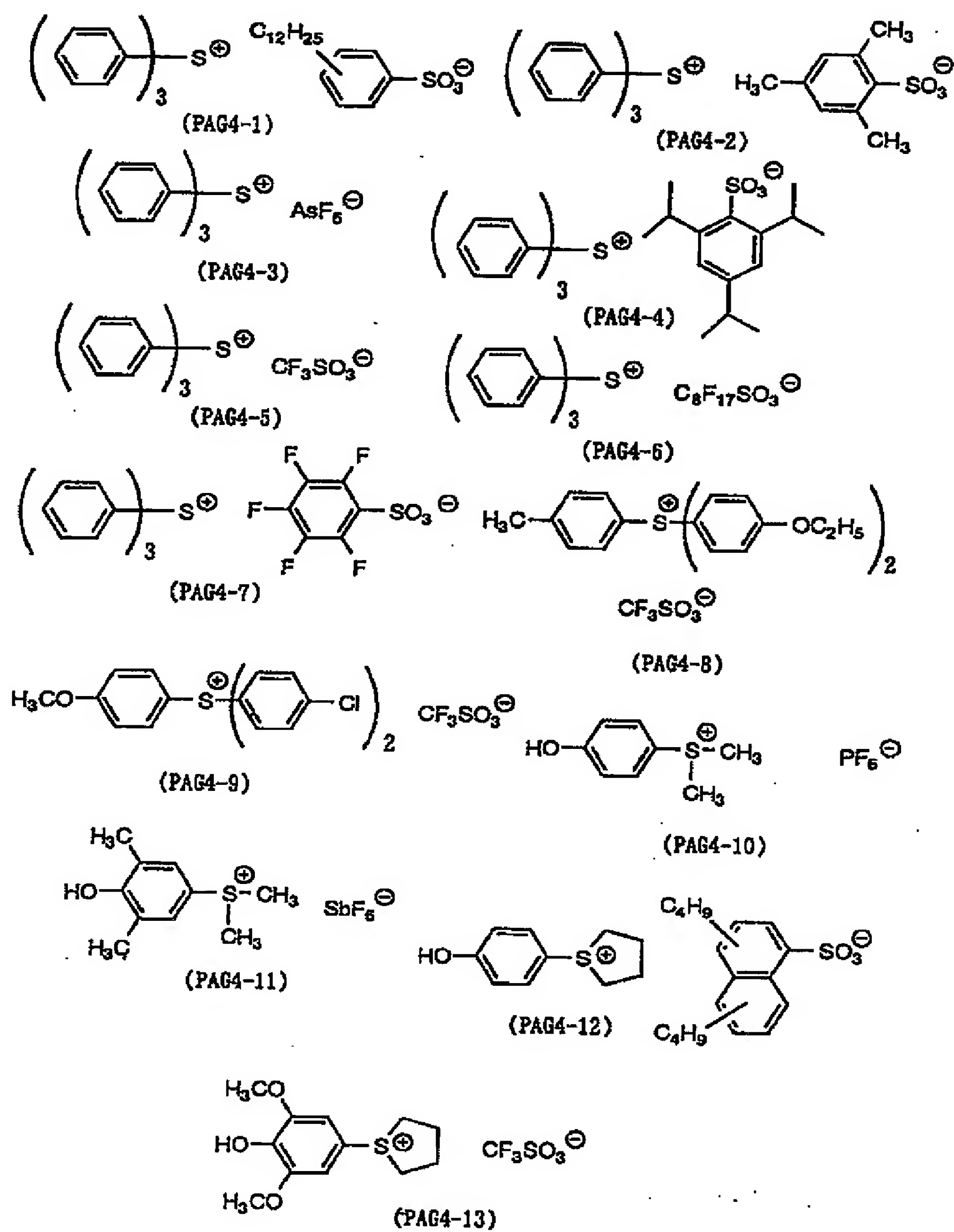
[0072]

[Formula 21]



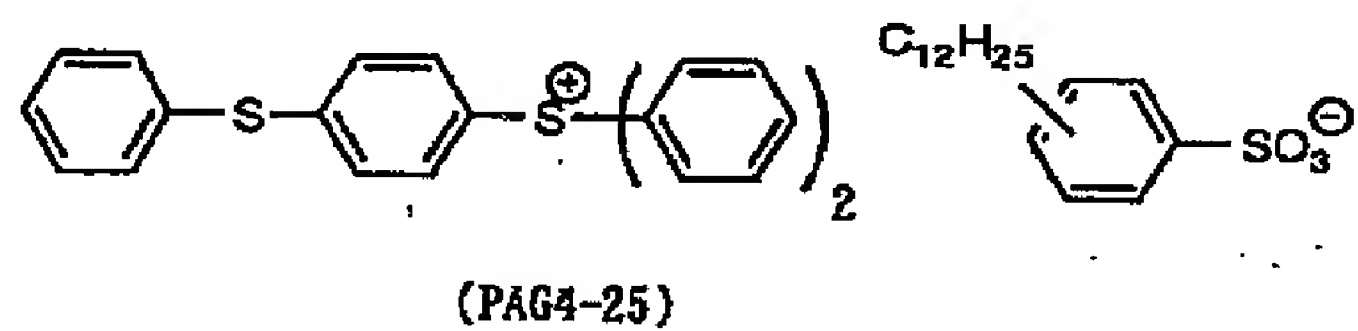
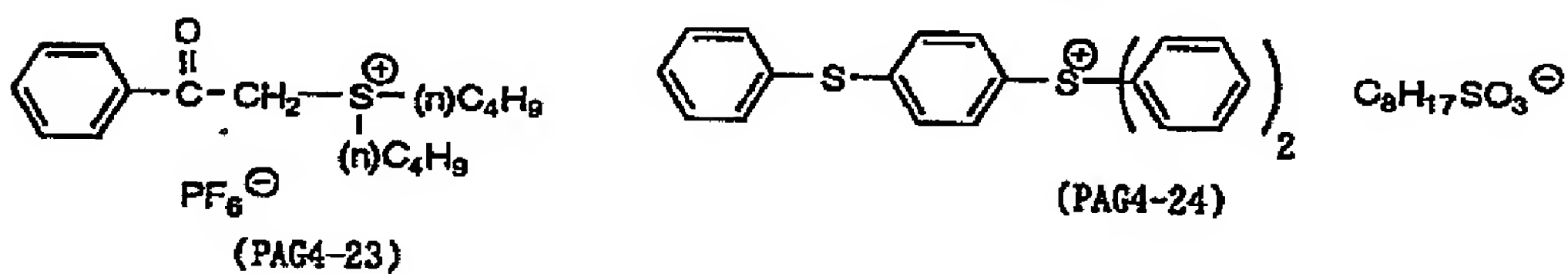
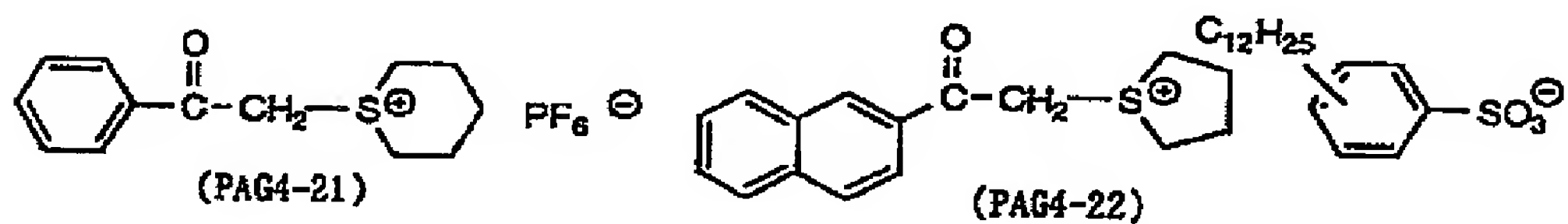
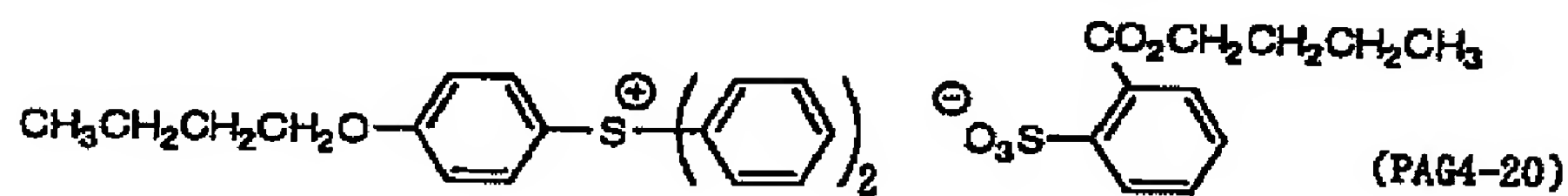
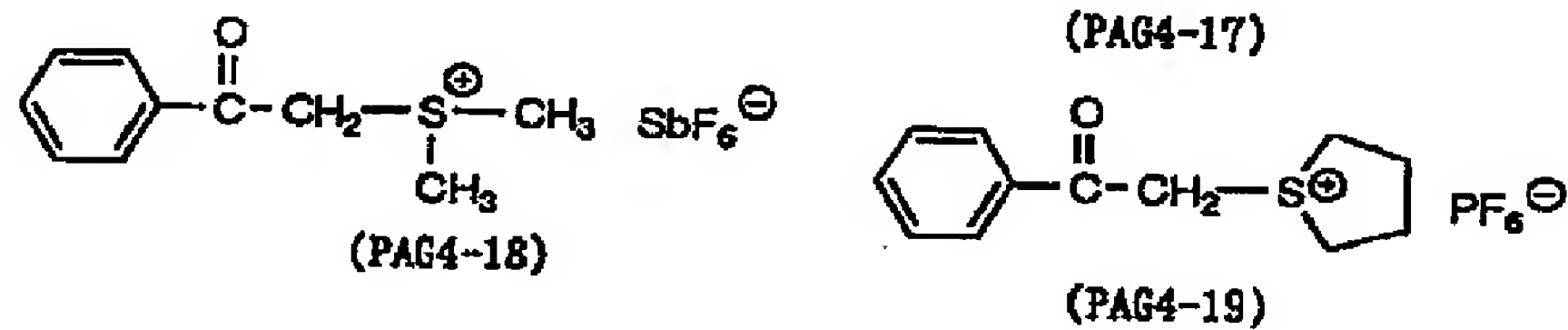
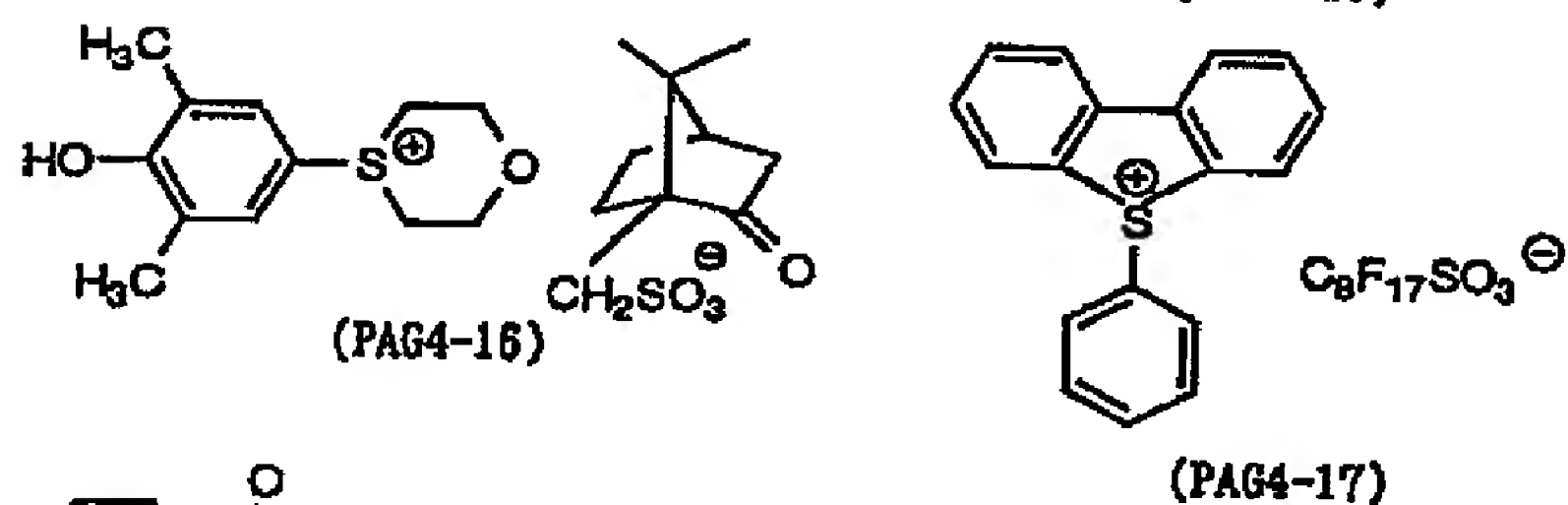
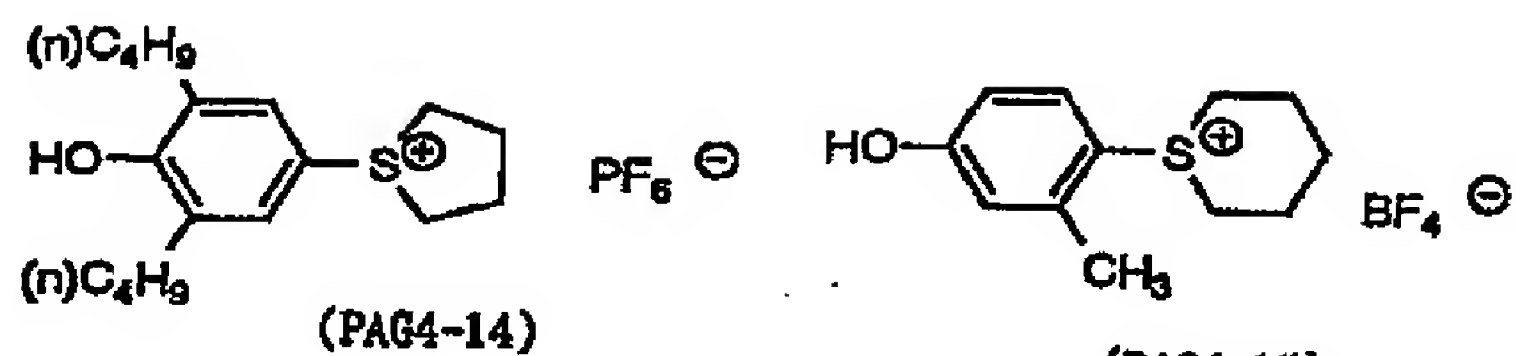
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[Formula 22]



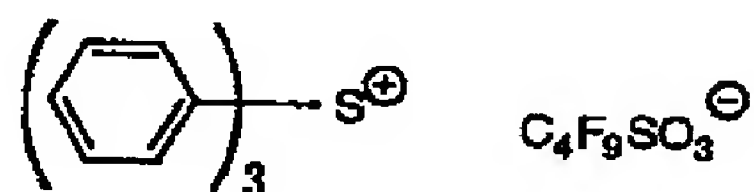
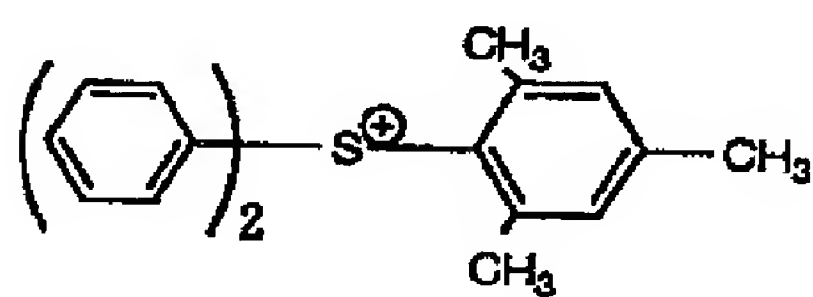
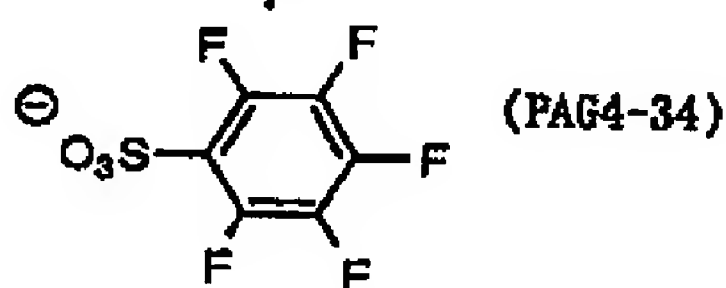
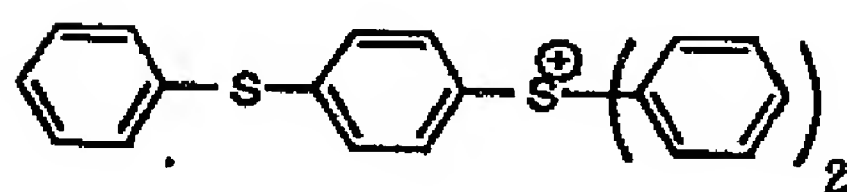
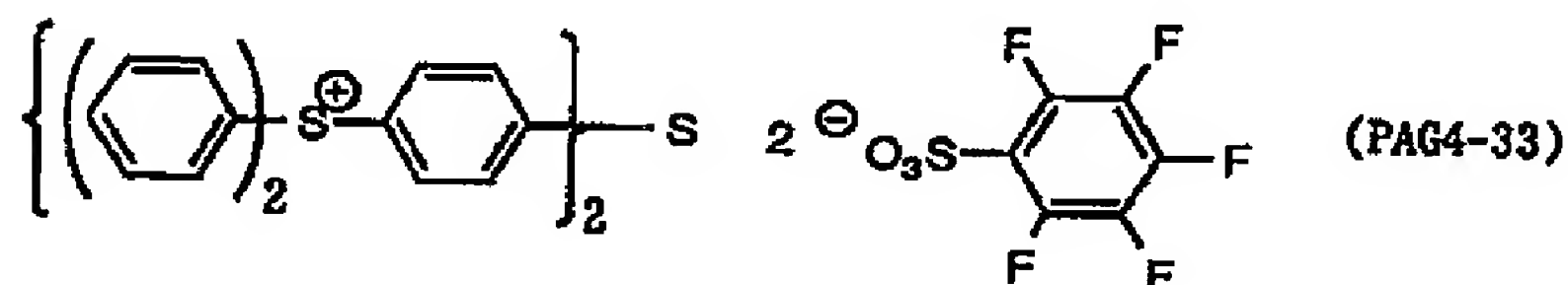
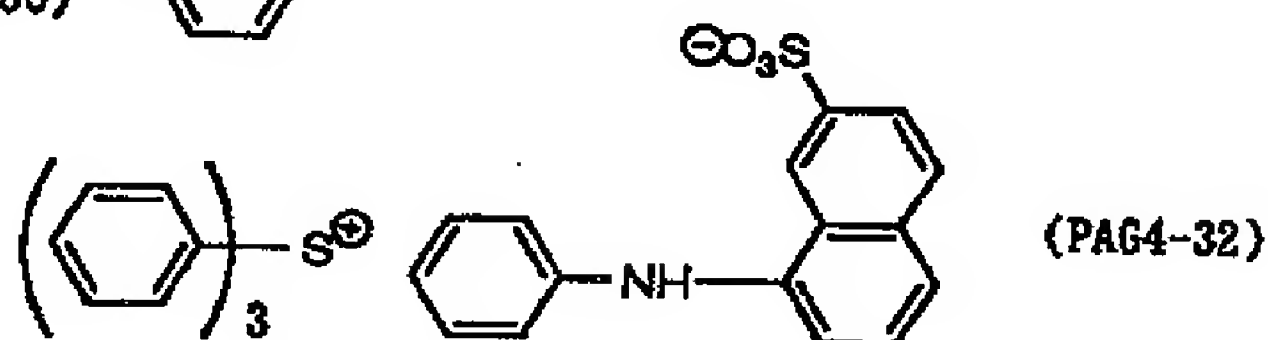
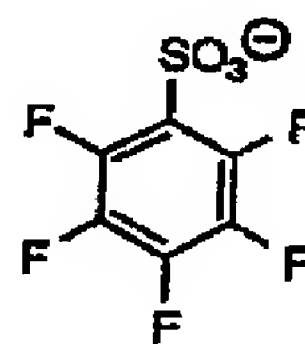
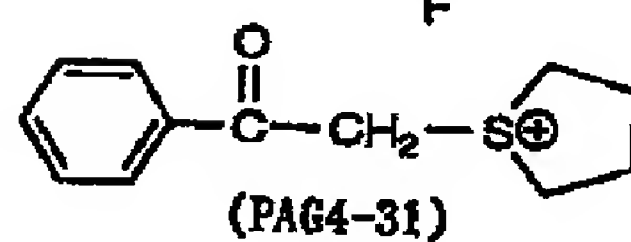
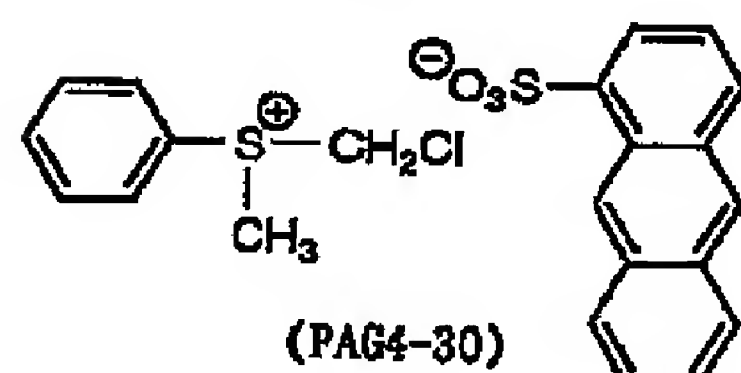
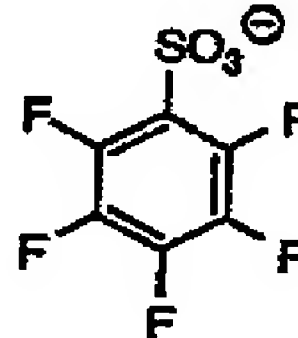
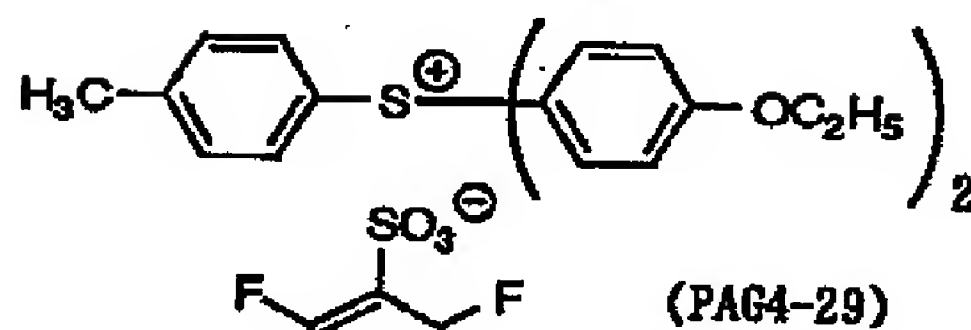
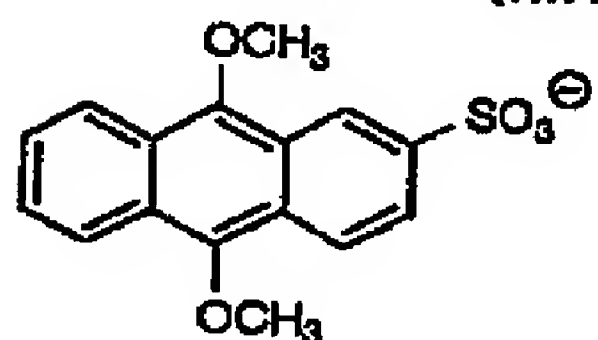
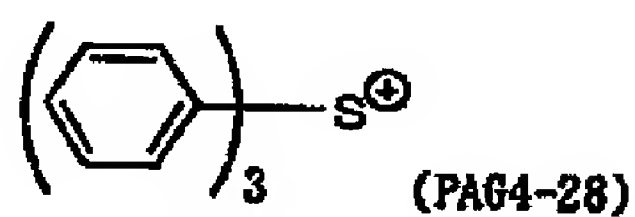
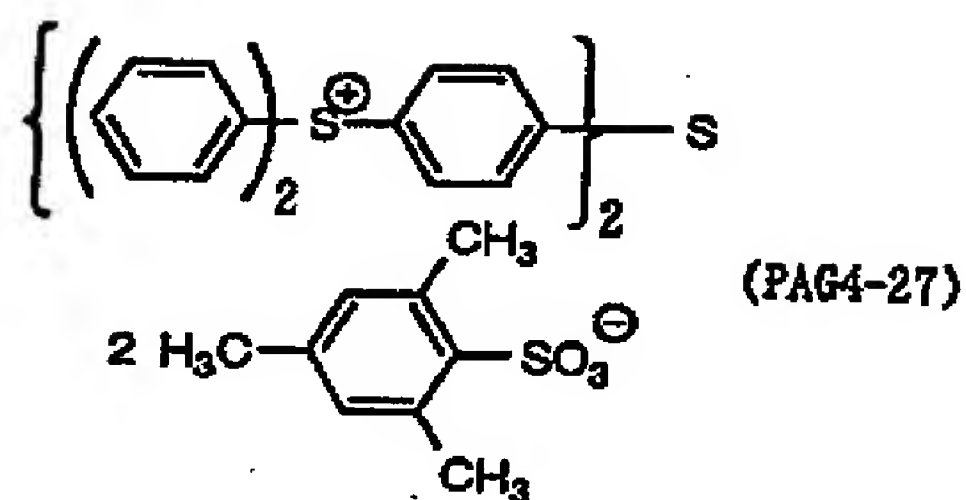
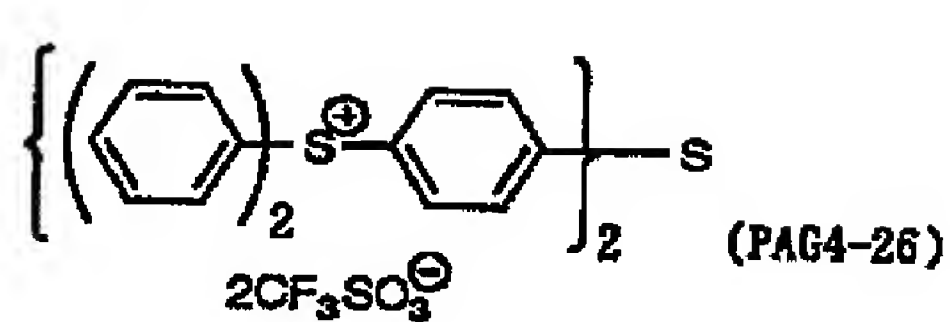
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[Formula 23]



[0075]

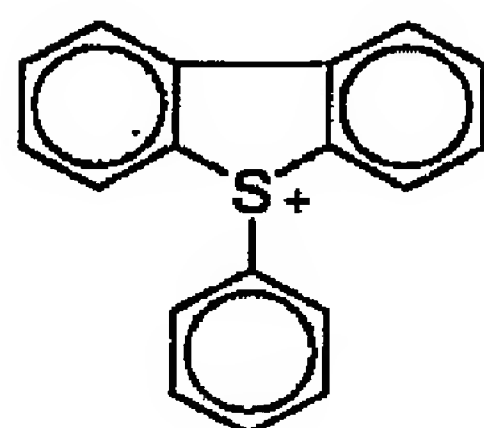
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[0076]

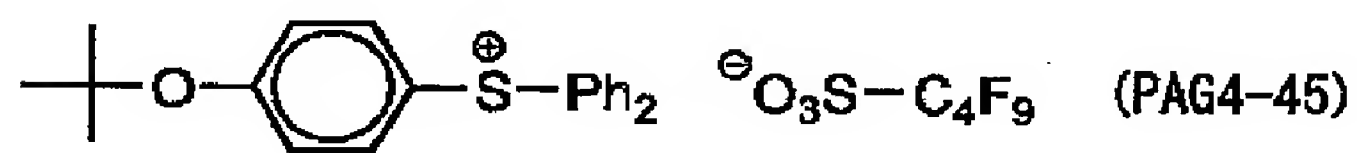
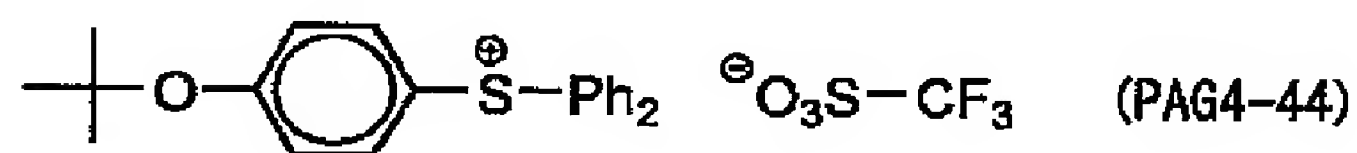
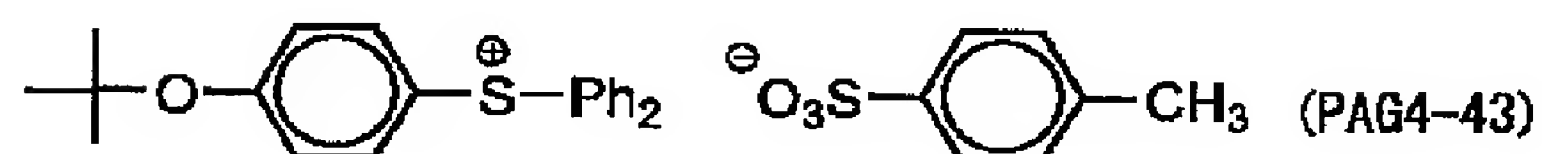
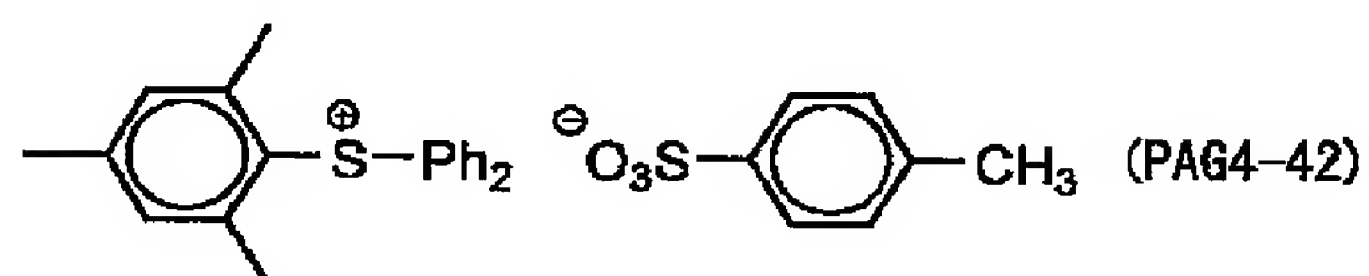
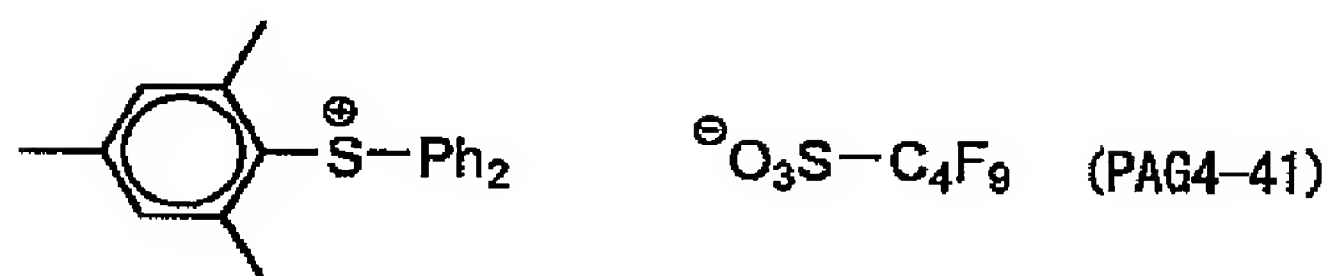
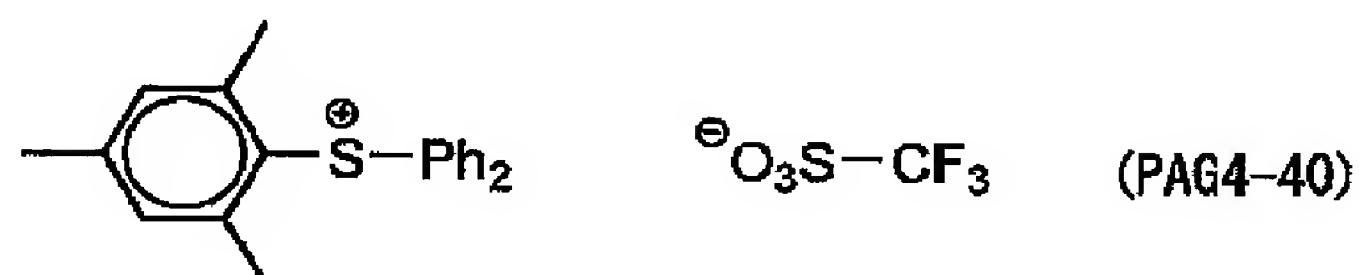
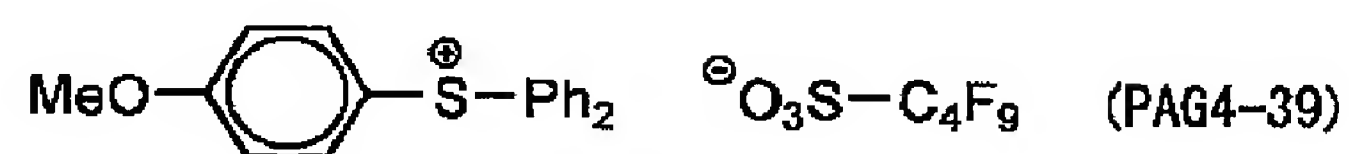
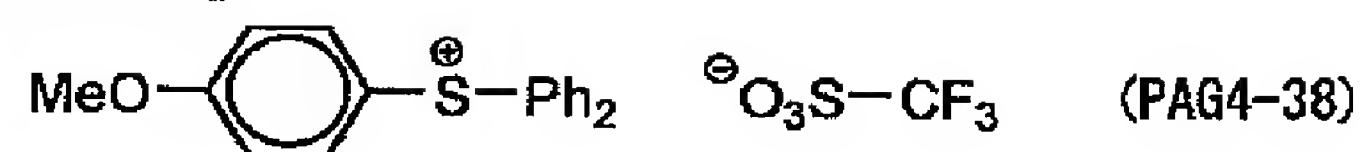
[Formula 25]

PAG4-37



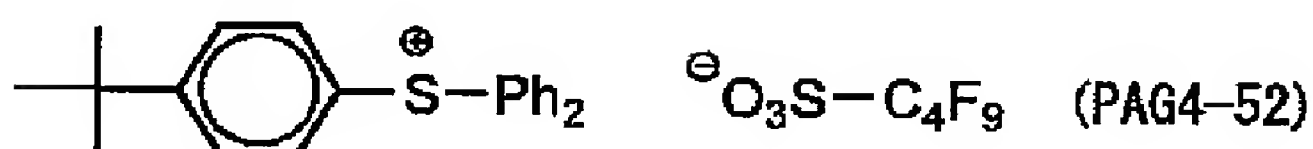
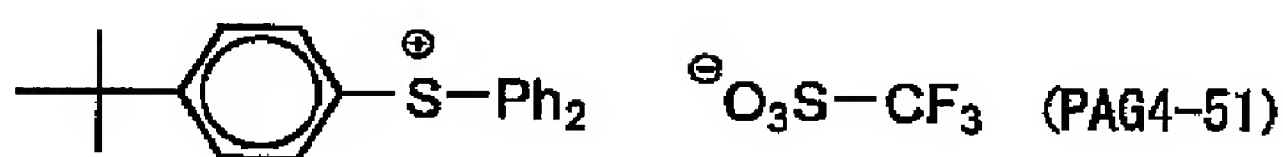
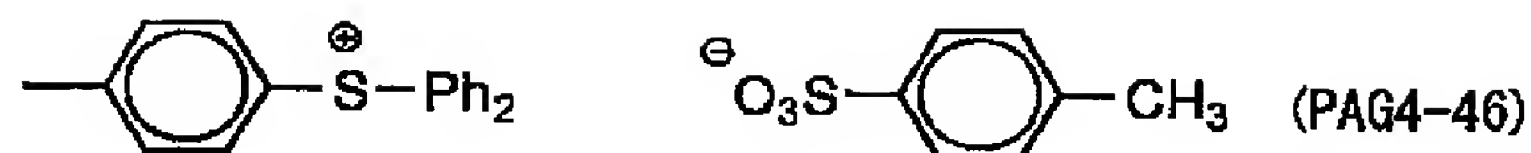
[0077]

[Formula 26]



[0078]

[Formula 27]

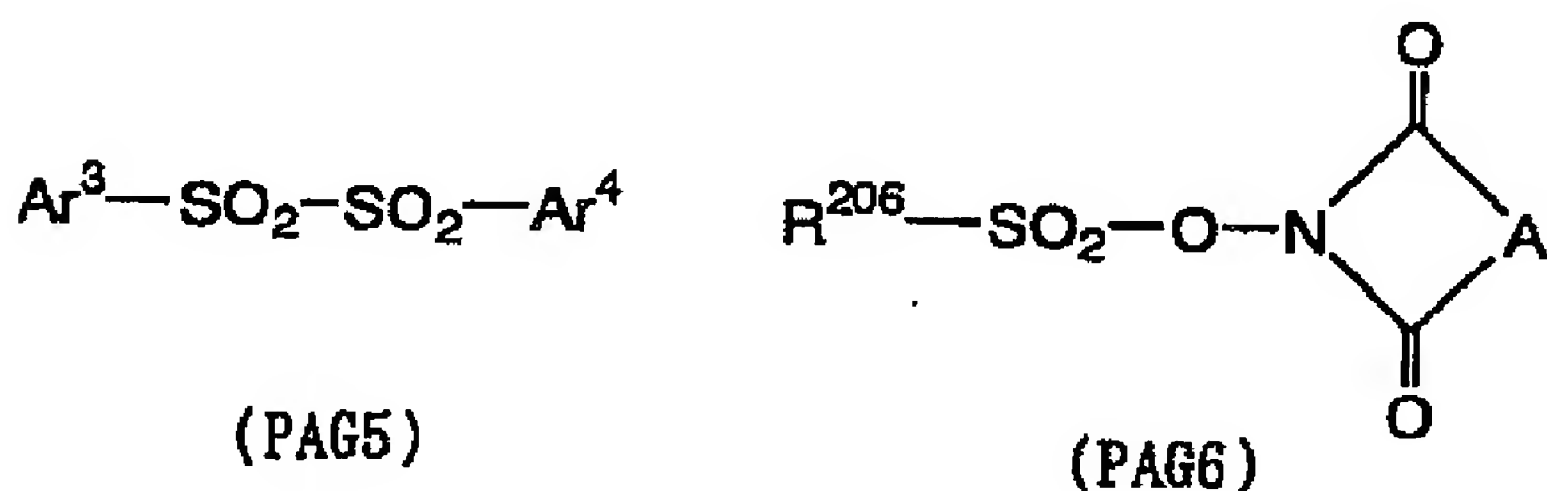


[0079] In the above, Ph expresses a phenyl group. The above-mentioned onium salt shown by the general formula (PAG3) and (PAG4) is well-known, for example, can be compounded by the approach of a publication to U.S. Pat. No. 2,807,648 and said 4,247,473 numbers, JP,53-101,331,A, etc.

[0080] (3) The imino sulfonate derivative expressed with the disulfon derivative or general formula (PAG6) expressed with the following general formula (PAG5).

[0081]

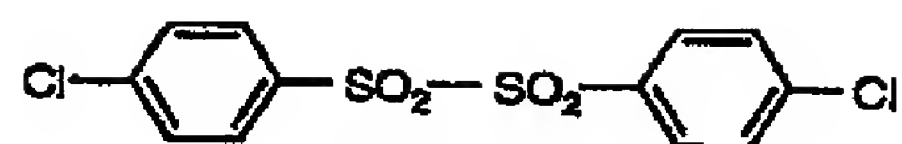
[Formula 28]



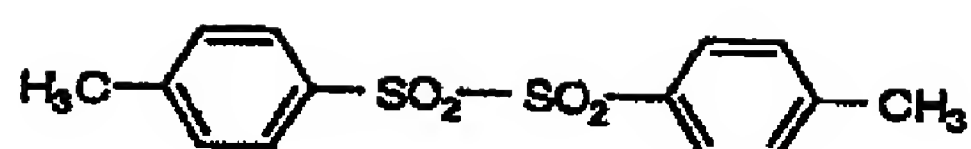
[0082] Ar3 and Ar4 show respectively the aryl group which is not permuted [a permutation or] independently among a formula. R206 shows the alkyl group which is not permuted [a permutation or] and an aryl group. A shows the alkylene group which is not permuted [a permutation or], an alkenylene group, and an arylene radical. Although the compound shown below as an example is mentioned, it is not limited to these.

[0083]

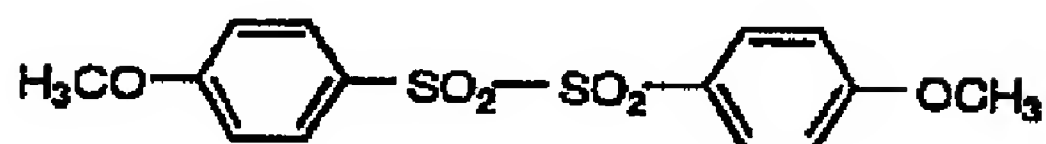
[Formula 29]



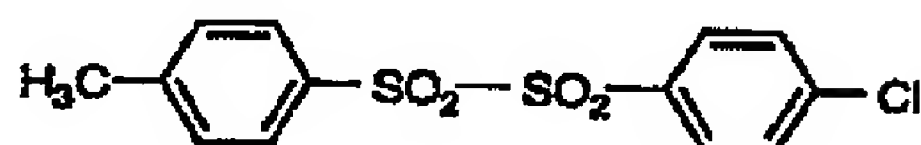
(PAG5-1)



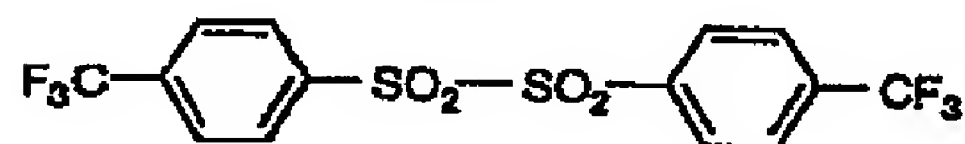
(PAG5-2)



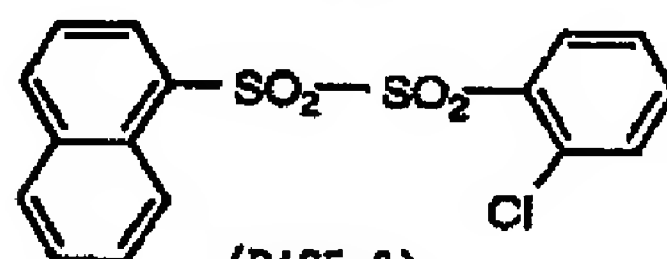
(PAG5-3)



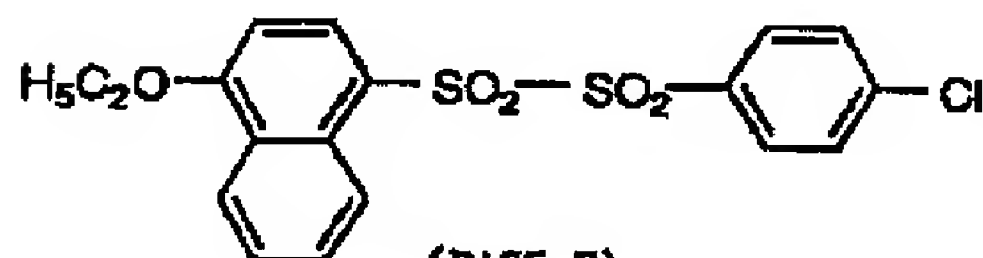
(PAG5-4)



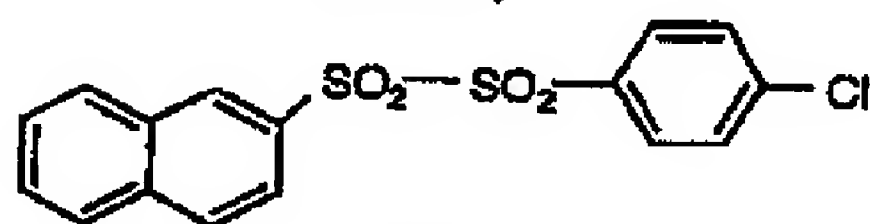
(PAG5-5)



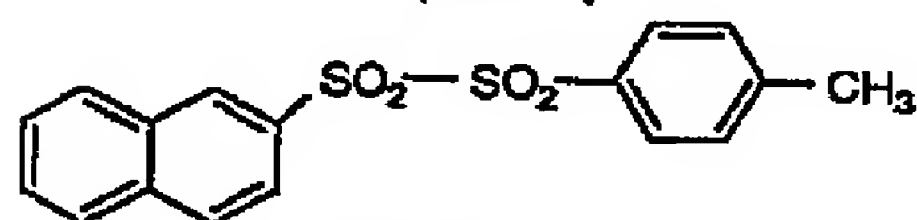
(PAG5-6)



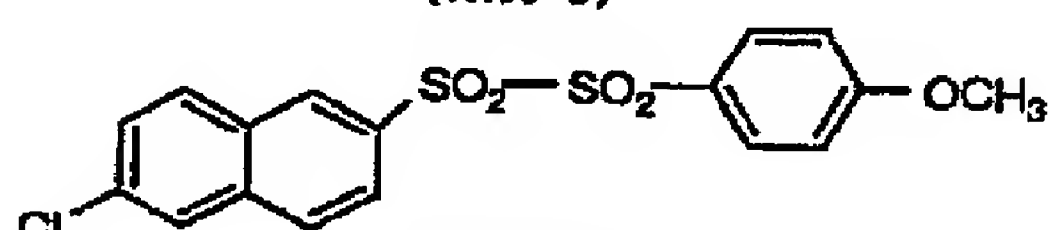
(PAG5-7)



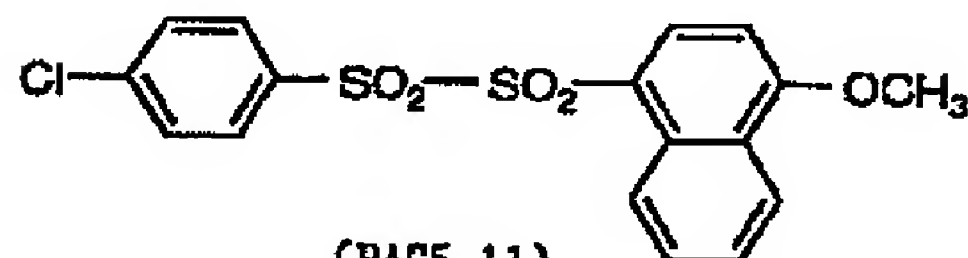
(PAG5-8)



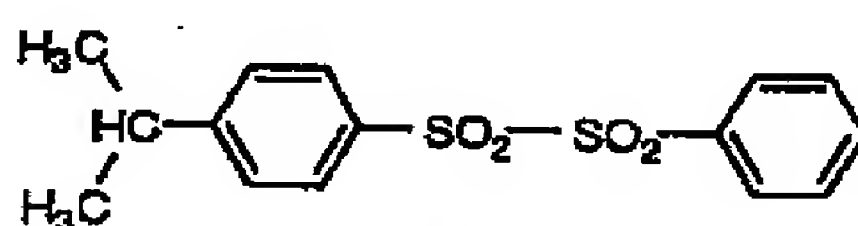
(PAG5-9)



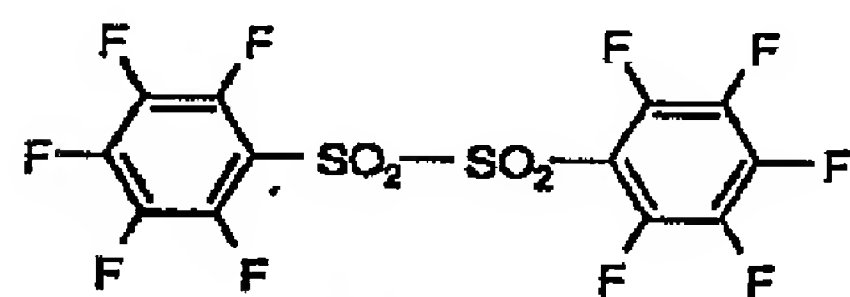
(PAG5-10)



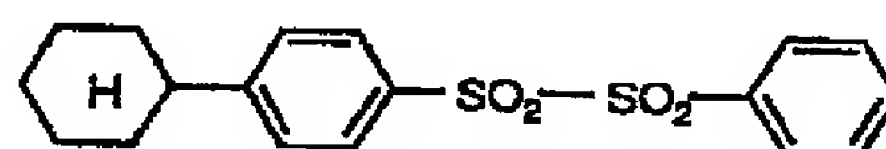
(PAG5-11)



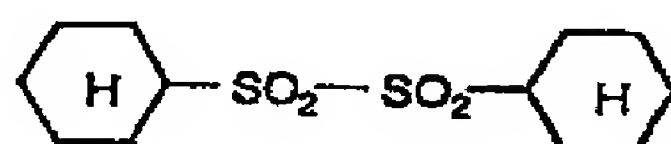
(PAG5-12)



(PAG5-13)



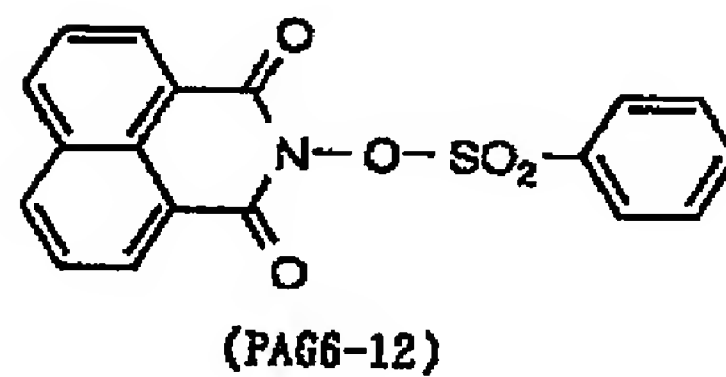
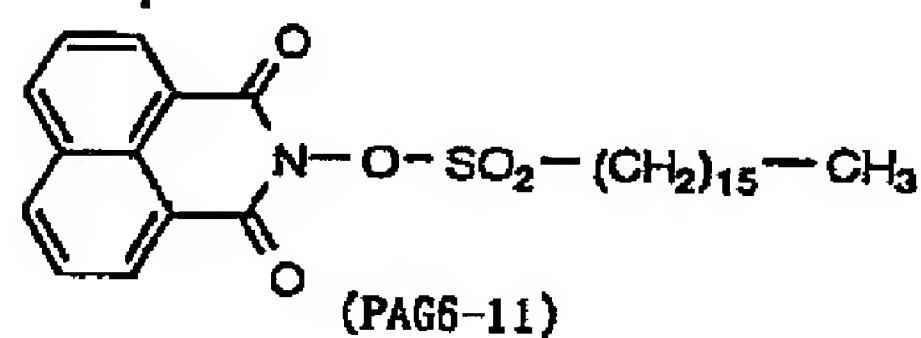
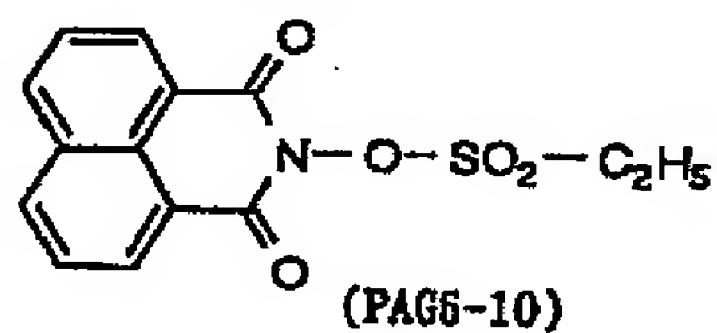
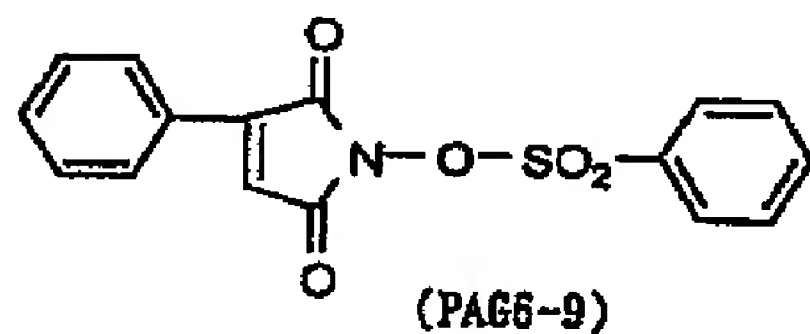
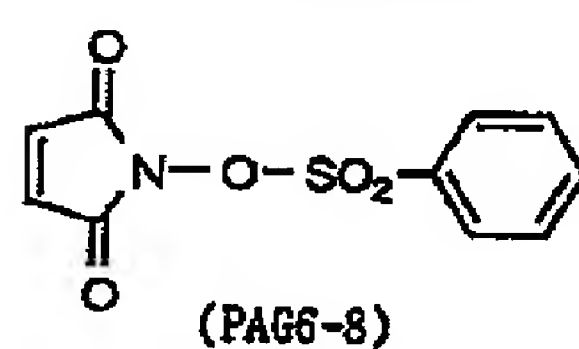
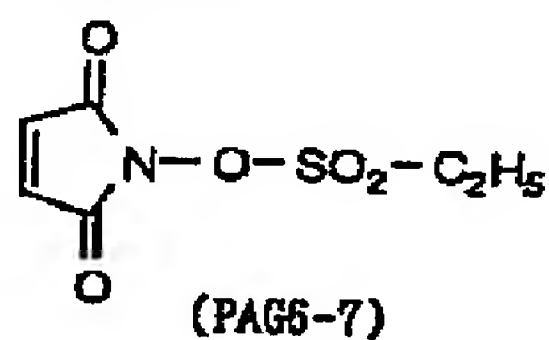
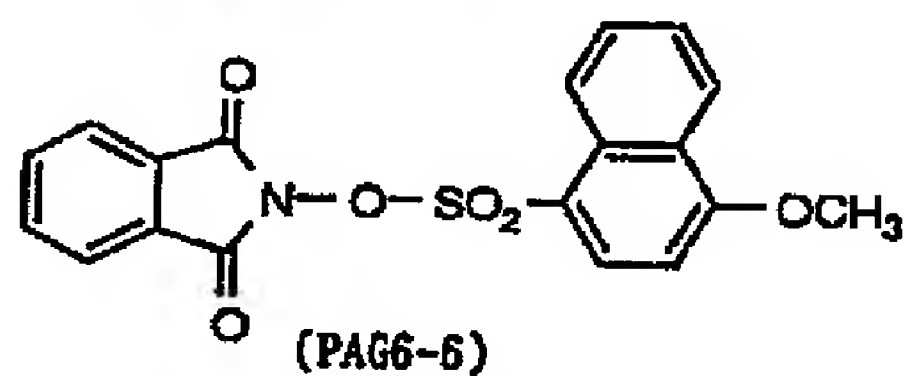
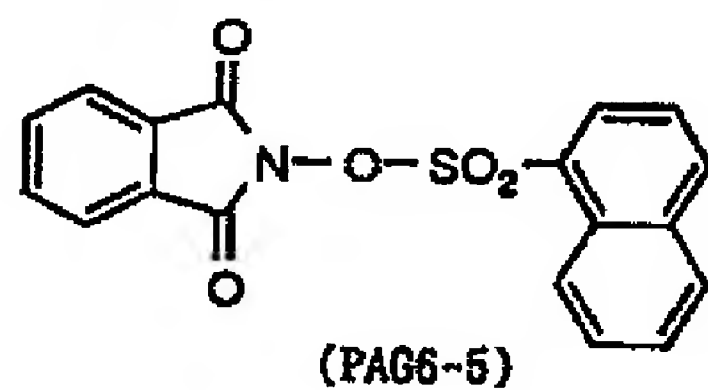
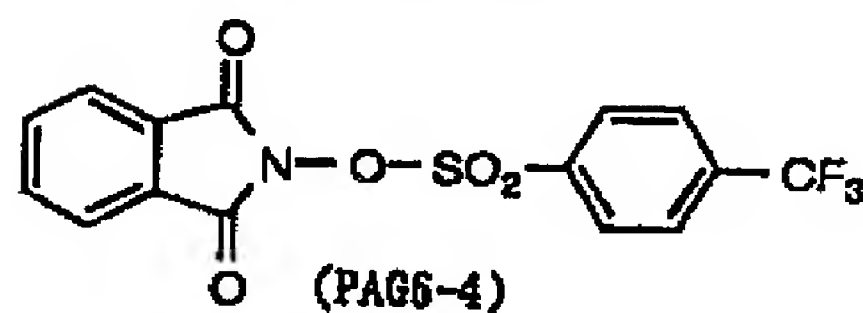
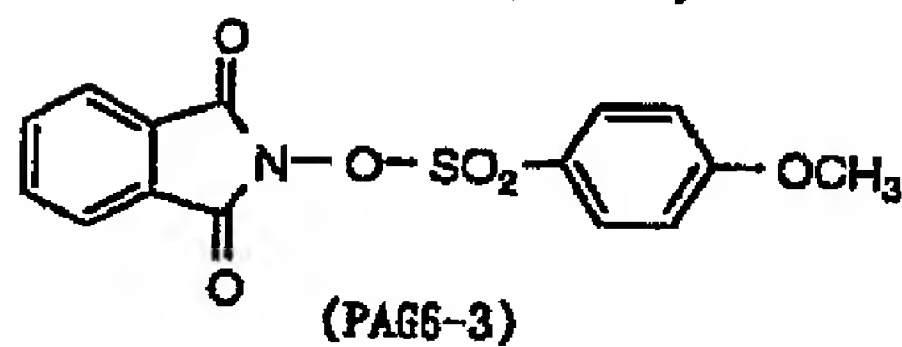
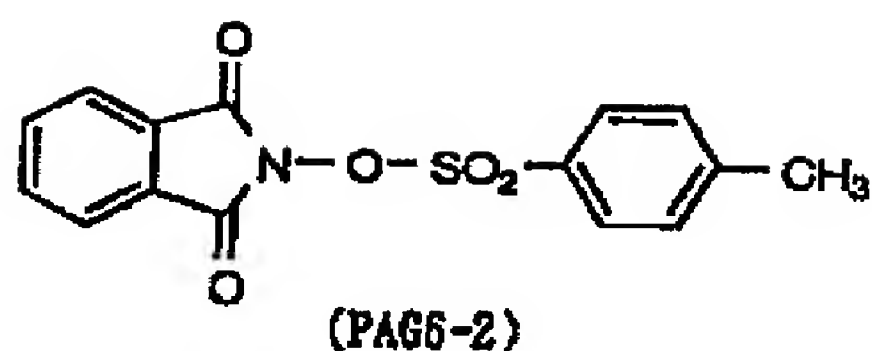
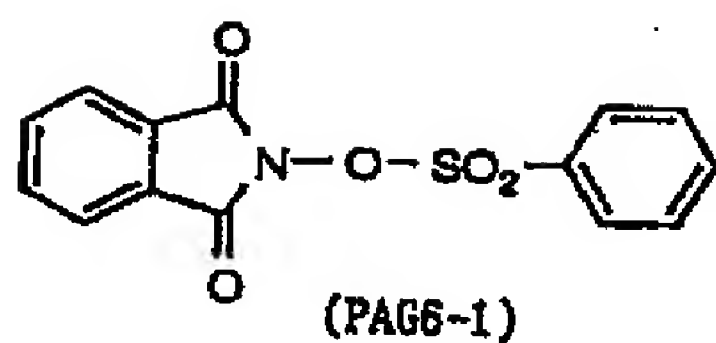
(PAG5-14)



(PAG5-15)

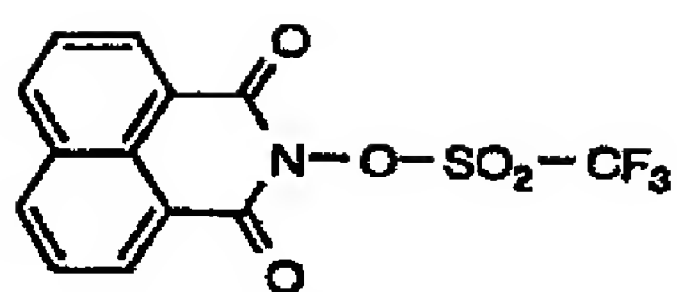
[0084]

[Formula 30]

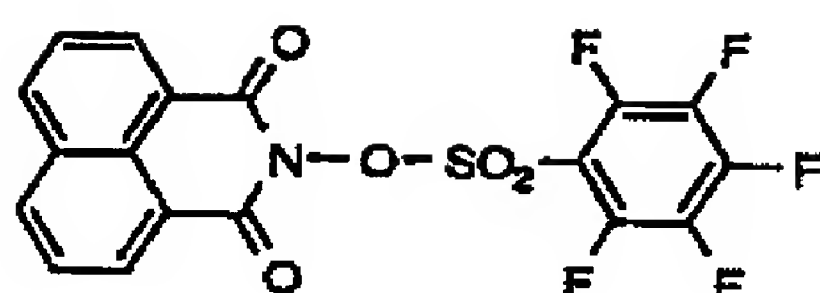


[0085]

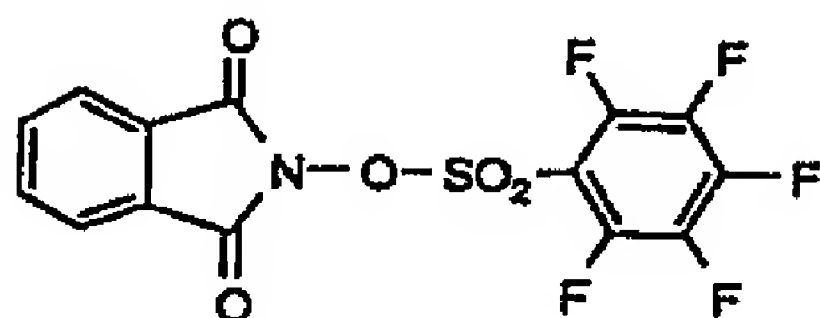
[Formula 31]



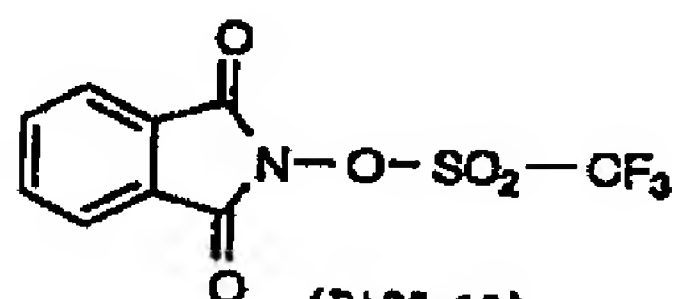
(PAG6-13)



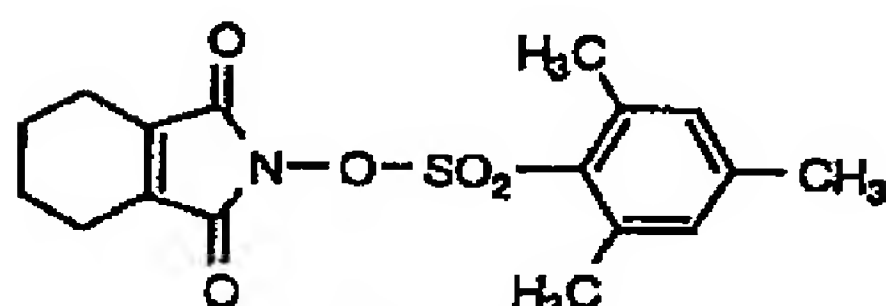
(PAG6-14)



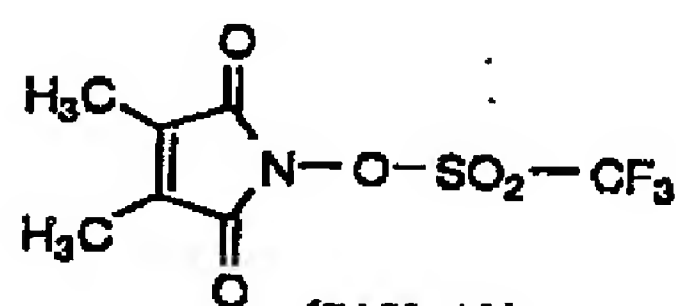
(PAG6-15)



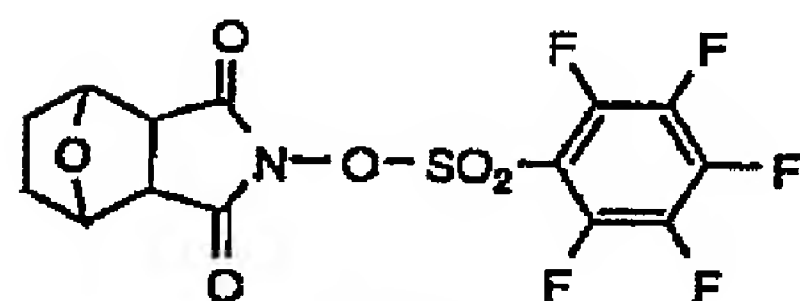
(PAG6-16)



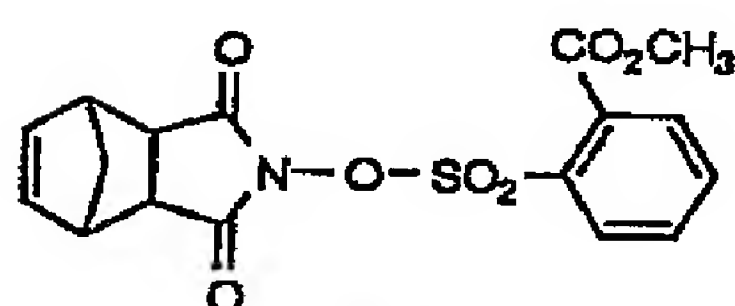
(PAG6-17)



(PAG6-18)



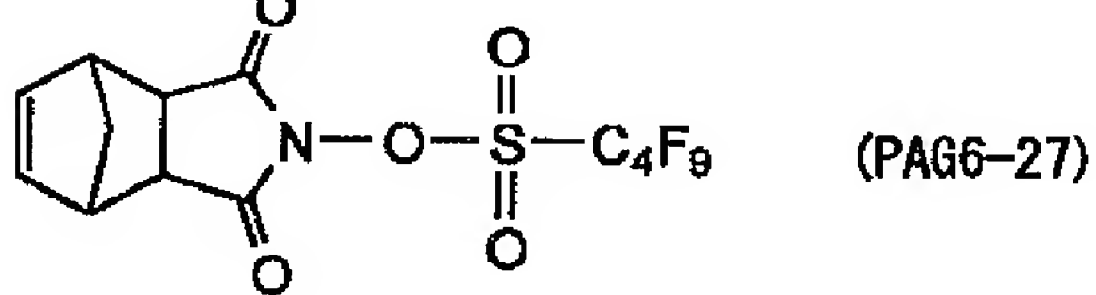
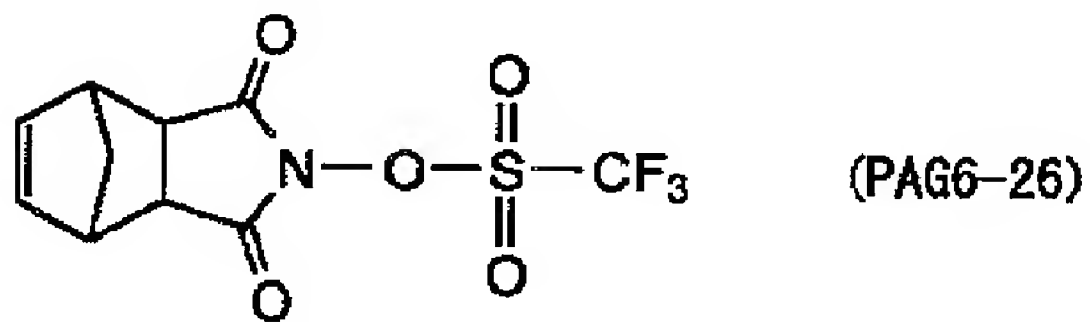
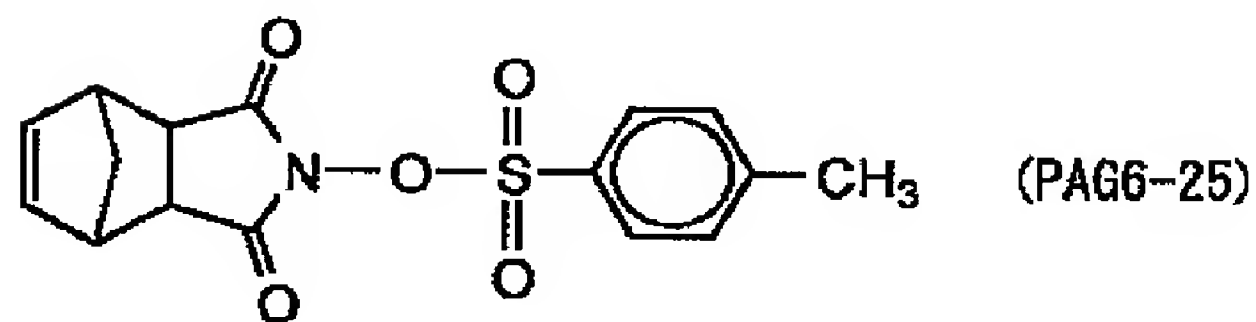
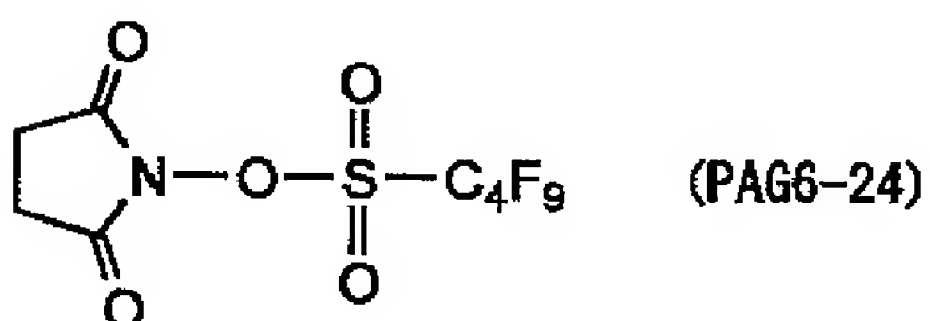
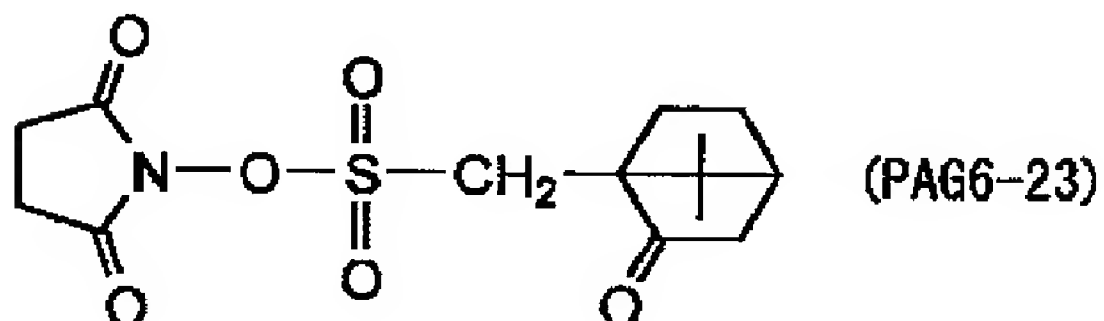
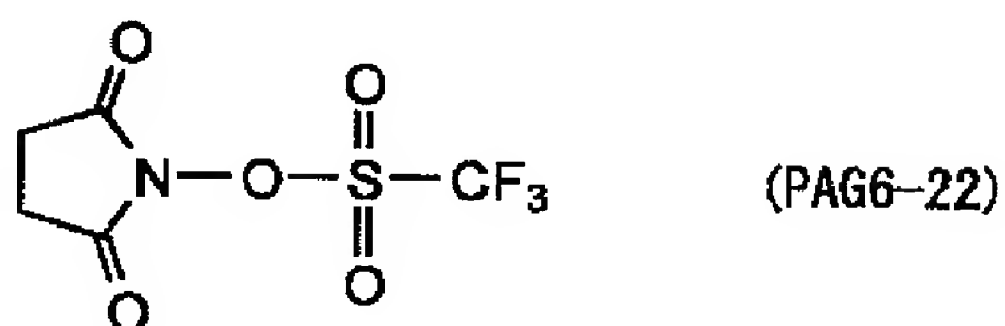
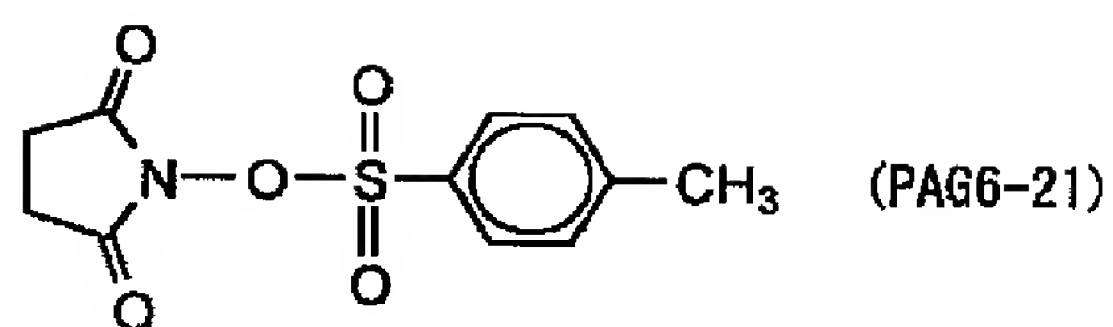
(PAG6-19)



(PAG6-20)

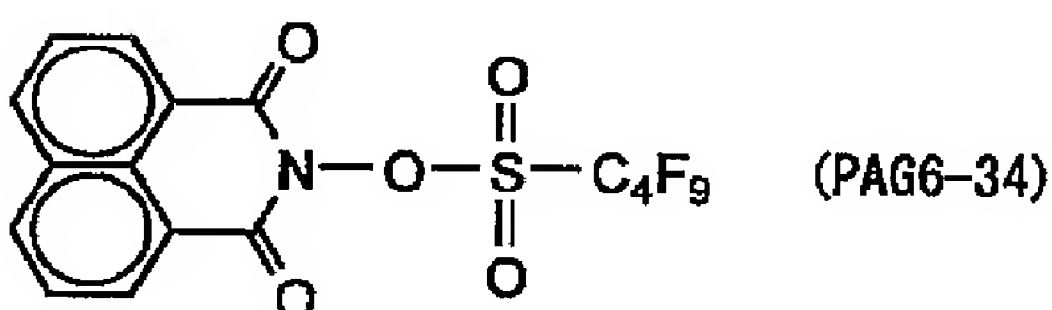
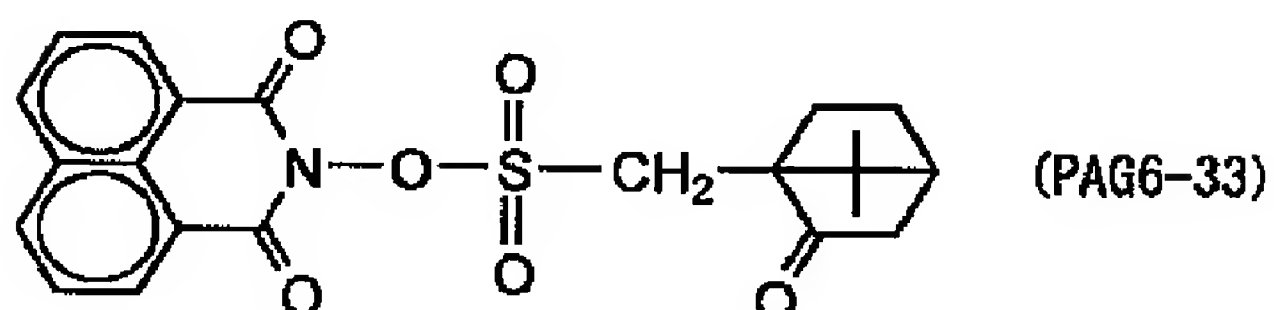
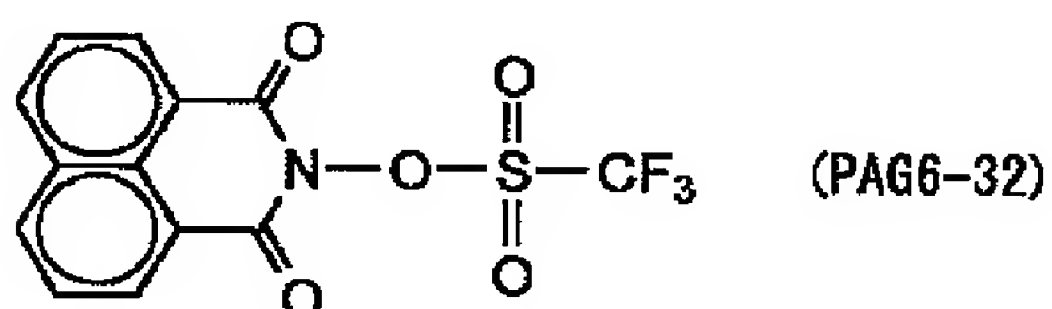
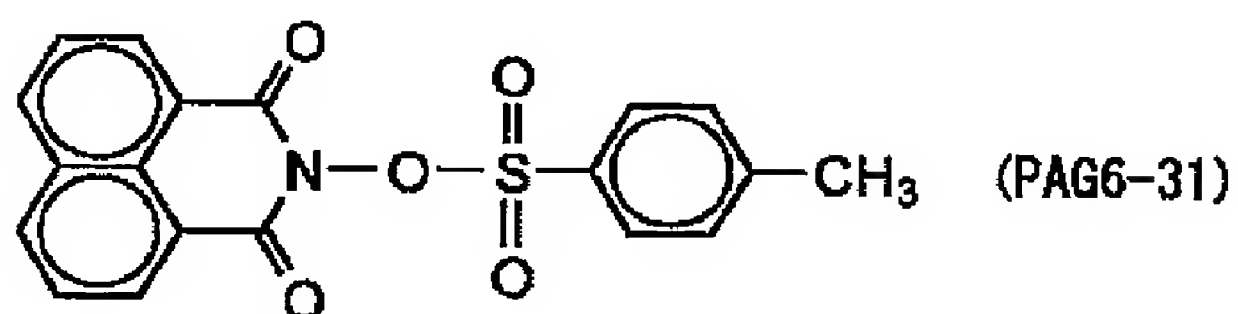
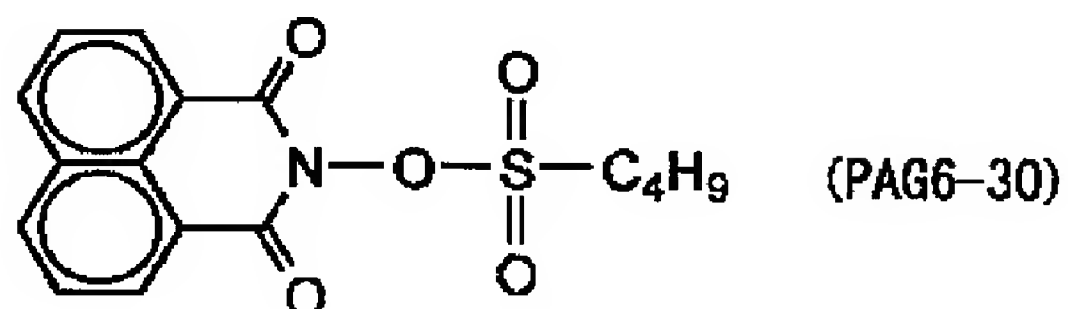
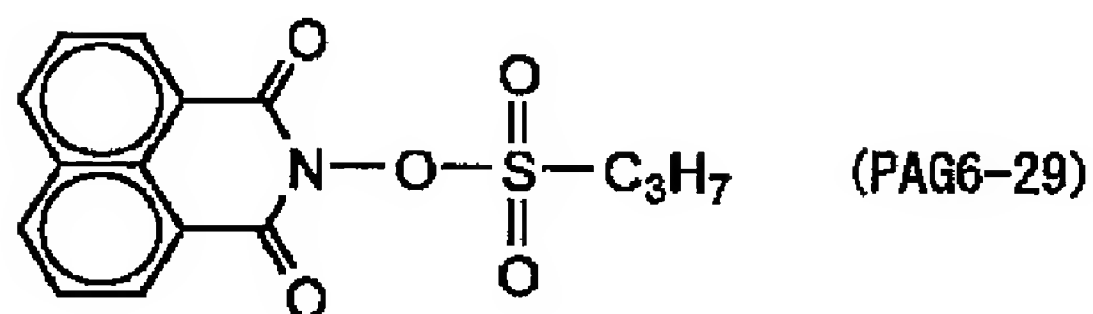
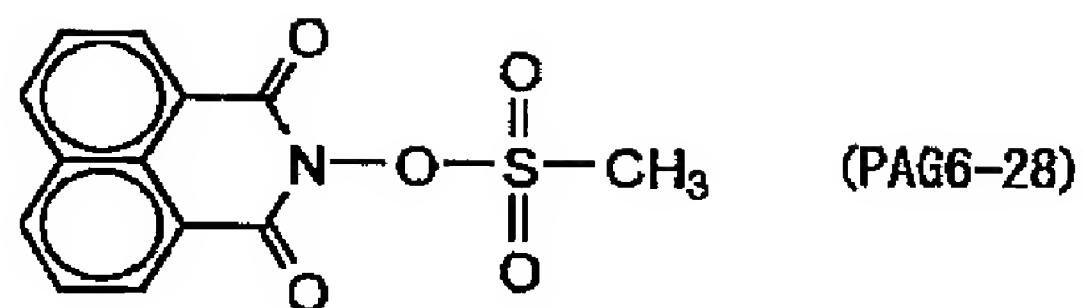
[0086]

[Formula 32]



[0087]

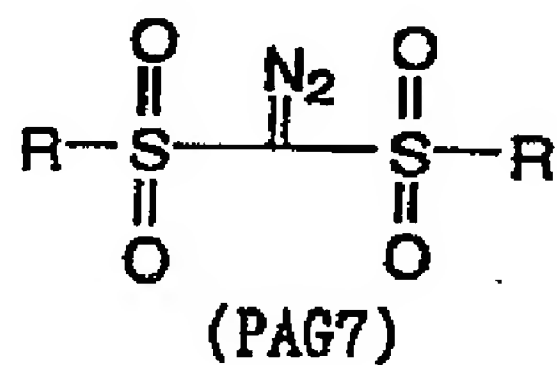
[Formula 33]



[0088] (4) The diazo disulfon derivative expressed with the following general formula (PAG7).

[0089]

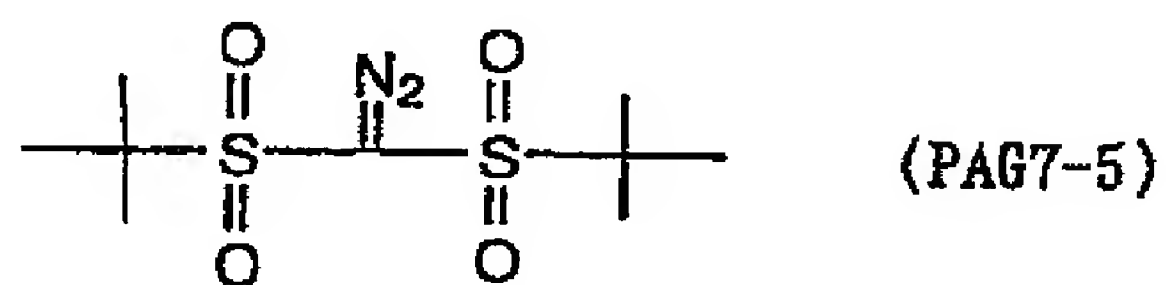
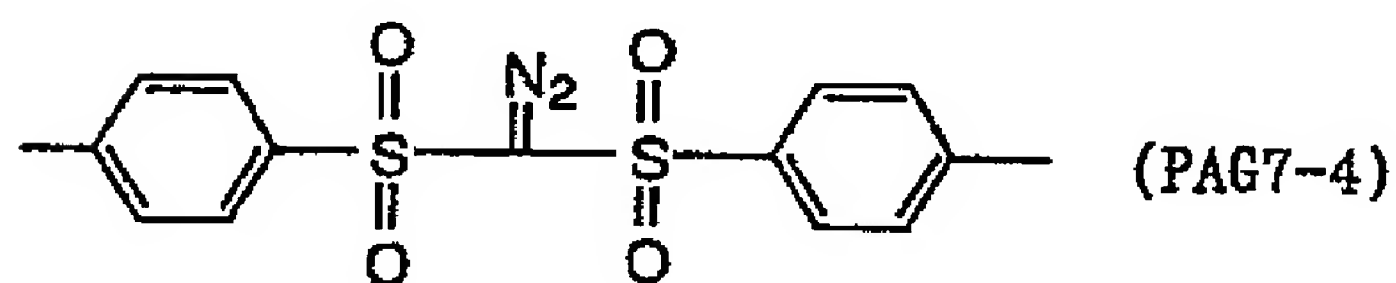
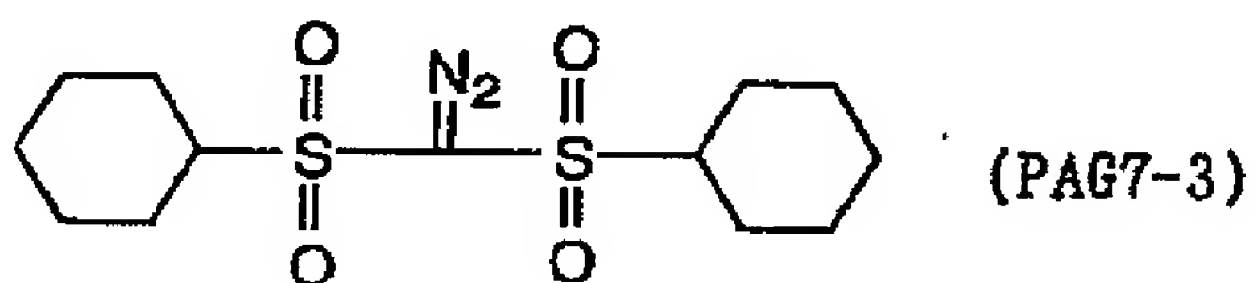
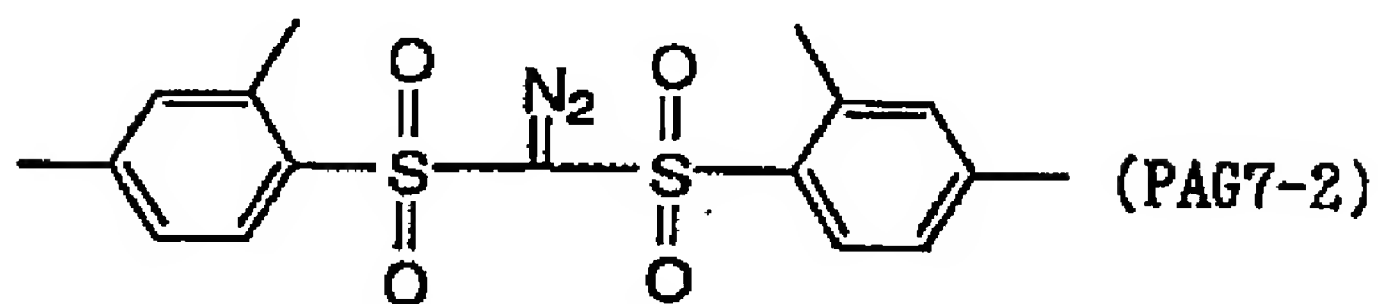
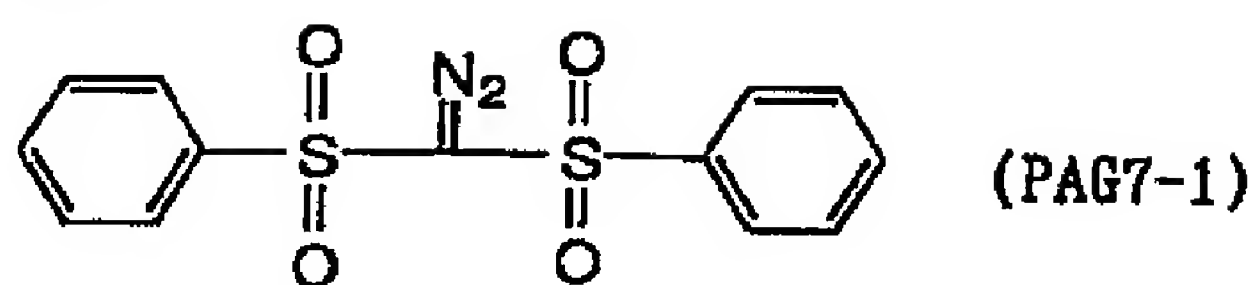
[Formula 34]



[0090] R expresses a straight chain, branching, an annular alkyl group, or the aryl group that may be permuted here. Although the compound shown below as an example is mentioned, it is not limited to these.

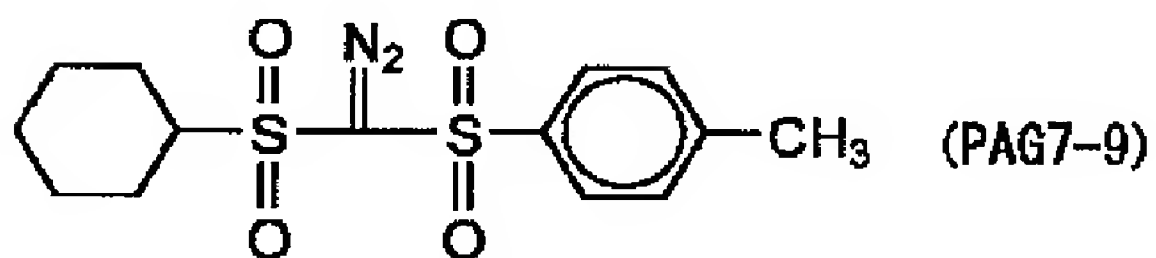
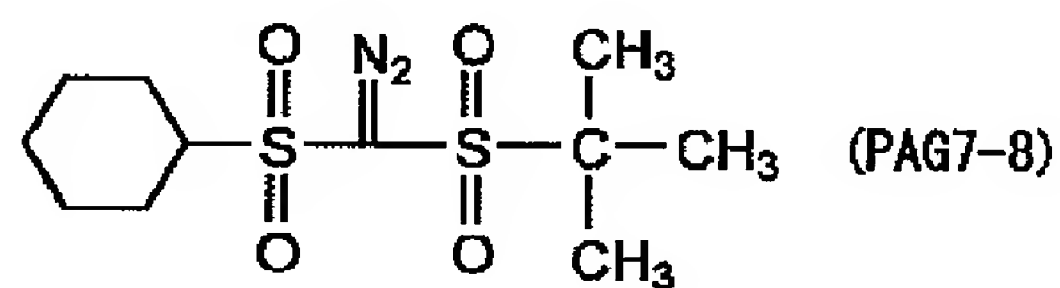
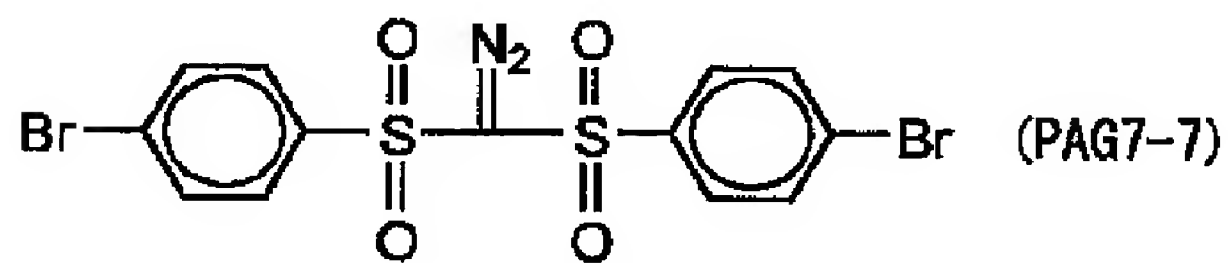
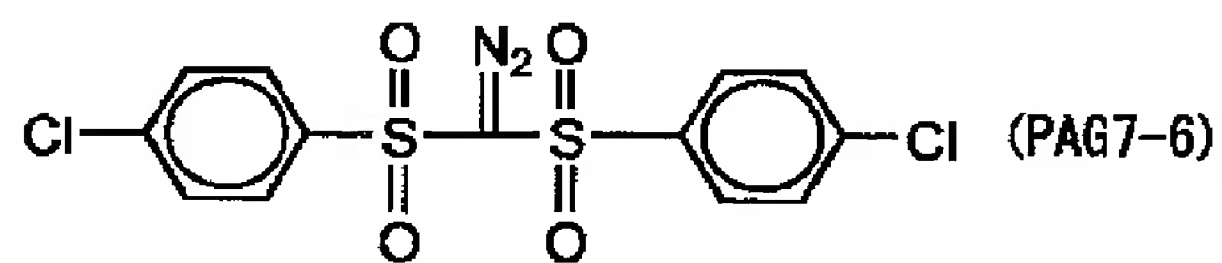
[0091]

[Formula 35]



[0092]

[Formula 36]



[0093] The addition of these photo-oxide generating agents is usually used in 0.01 – 30% of the weight of the

range on the basis of the solid content in a constituent, and is preferably used in 0.5 – 10% of the weight of the range still more preferably 0.3 to 20% of the weight. The addition of a photo-oxide generating agent becomes [if fewer than 0.01 % of the weight, will become the inclination for sensibility to become low and if there are more additions than 30 % of the weight, the light absorption of a resist will become high too much and / aggravation of a profile and a process (especially BEKU) margin] narrow and is not desirable.

[0094] [3] Desirable (D) organic base nature compound which can be used by (D) organic base nature compound this invention is a compound with basicity stronger than a phenol. A nitrogen-containing basicity compound is desirable especially.

(D) By adding an organic base nature compound, the sensibility fluctuation by the passage of time is improved. For example, the compound which has the following structure as a (D) organic base nature compound can be mentioned.

[0095]

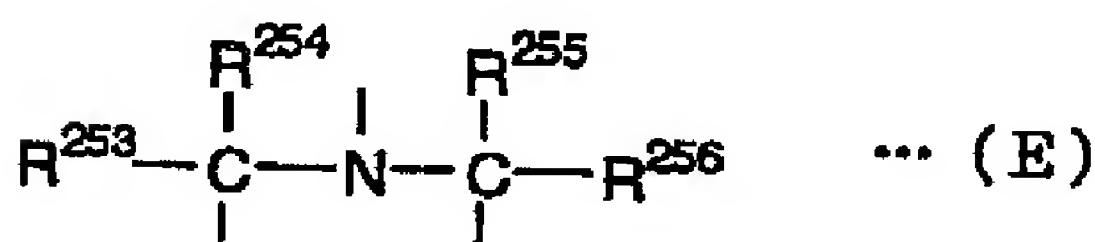
[Formula 37]



[0096] R250, R251, and R252 are the permutations or the unsubstituted aryl groups of a hydrogen atom, the alkyl group of carbon numbers 1–6, the amino alkyl group of carbon numbers 1–6, the hydroxyalkyl radical of carbon numbers 1–6, or carbon numbers 6–20 independently respectively, it may join together mutually and R251 and R252 may form a ring here.

[0097]

[Formula 38]



[0098] (R253, R254, R255, and R256 show the alkyl group of carbon numbers 1–6 independently respectively among a formula)

Furthermore, a desirable compound is a nitrogen-containing basicity compound which has two or more nitrogen atoms of different chemical environment in a monad, and is a compound which has especially a compound or alkylamino radical including both ring structures containing the amino group and nitrogen atom

which are not permuted [a permutation or] preferably. As a desirable example, the aminopyridine which is not permuted [the guanidine which is not permuted / a permutation or / a permutation, or], The amino pyrrolidine which is not permuted [the amino alkyl pyridine which is not permuted / a permutation or / a permutation, or], The pyrazole which is not permuted [in DAZORU which is not permuted / a permutation or /, a permutation or], The pyrimidine which is not permuted [the pyrazine which is not permuted / a permutation or /, a permutation, or], The amino alkyl morpholine which is not permuted [the amino morpholine which is not permuted / the piperazine which is not permuted / the pyrazoline which is not permuted / the imidazoline which is not permuted / the pudding which is not permuted / a permutation or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or] is mentioned. Desirable substituents are the amino group, an amino alkyl group, an alkylamino radical, an amino aryl group, an arylamino radical, an alkyl group, an alkoxy group, an acyl group, an acyloxy radical, an aryl group, an aryloxy group, a nitro group, a hydroxyl group, and a cyano group.

[0099] As a desirable example of a nitrogen-containing basicity compound, guanidine, 1, and 1-dimethyl guanidine, 1, 1, 3, 3, - tetramethyl guanidine, 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, 2-dimethylamino pyridine, 4-dimethylaminopyridine, 2-diethylamino pyridine, 2-(aminomethyl) pyridine, 2-amino-3-methylpyridine, 2-amino-4-methylpyridine, 2-amino-5-methylpyridine, 2-amino-6-methylpyridine, 3-aminoethyl pyridine, 4-aminoethyl pyridine, 3-amino pyrrolidine, A piperazine, N-(2-aminoethyl) piperazine, N-(2-aminoethyl) piperidine, 4-amino - 2, 2, 6, and 6-tetramethylpiperidine, 4-piperidino piperidine, A 2-imino piperidine, 1-(2-aminoethyl) pyrrolidine, a pyrazole, 3-amino-5-methyl pyrazole, 5 - Amino-3-methyl-1-p-tolyl pyrazole, Pyrazine, 2-(aminomethyl)-5-methyl pyrazine, a pyrimidine, 2, 4-diamino pyrimidine, 4, 6-dihydroxy pyrimidine, 2-pyrazoline, 3-pyrazoline, N-amino morpholine, N-(2-aminoethyl) morpholine, 1, a 5-diazabicyclo [4.3.0] nona-5-en, 1, a 8-diazabicyclo [5.4.0] undeca-7-en, 1 and 4-diazabicyclo [2.2.2] octane, 2 and 4, 5-triphenyl imidazole, N-methyl morpholine, N-ethyl morpholine, N-hydroxyethyl morpholine, The 3rd class morpholine derivatives, such as N-benzyl morpholine and cyclohexyl morpholino ethyl thiourea (CHMETU), Although the hindered amine (for example, thing given in this official report [0005]) of a publication is mentioned to JP,11-52575,A, it is not limited to this.

[0100] Especially a desirable example 1, a 5-diazabicyclo [4.3.0] nona-5-en, 1, a 8-diazabicyclo [5.4.0] undeca-7-en, 1, 4-diazabicyclo [2.2.2] octane, 4-dimethylaminopyridine, hexamethylenetetramine, 4, and 4-dimethyl imidazoline, Hindered amine, such as the 3rd class morpholines, such as pyrroles, pyrazoles, imidazole derivatives, pyridazines, pyrimidines, and CHMETU, and bis(1, 2, 2, 6, and 6-pentamethyl-4-piperidyl) SEBAGETO, can be mentioned. Especially, 1, 5-diazabicyclo [4.3.0] nona-5-en, 1, 8-diazabicyclo [5.4.0] undeca-7-en, 1, and 4-diazabicyclo [2.2.2] octane, 4-dimethylaminopyridine, a hexamethylenetetramine, CHMETU, and bis(1, 2, 2, 6, and 6-pentamethyl-4-piperidyl) SEBAGETO are desirable.

[0101] These organic base nature compounds are independent, or are combined two or more sorts and used. The amount of the organic base nature compound used is usually 0.01 - 5 % of the weight preferably 0.001 to 10% of the weight to the solid content of all the constituents of a photopolymer constituent. At less than 0.001 % of the weight, the effectiveness of addition of the above-mentioned organic base nature compound is not acquired. On the other hand, when it exceeds 10 % of the weight, there is an inclination for the

development nature of the fall of sensibility or a non-exposed area to get worse.

[0102] [4] In the positive type photoresist constituent of (F) fluorine system and/or silicon system surface-active-agent this invention, a fluorine system and/or a silicon system surface active agent are contained preferably. It is desirable to contain either of the surfactants containing both a fluorochemical surfactant, a silicon system surfactant and a fluorine atom, and a silicon atom or two sorts or more in the positive type photoresist constituent of this invention. When the positive type photoresist constituent of this invention contains the above-mentioned acidolysis nature resin and the above-mentioned surfactant, a dependency of condensation and rarefaction is improved.

[0103] As these surfactants, for example, JP,62-36663,A, JP,61-226746,A, JP,61-226745,A, JP,62-170950,A, JP,63-34540,A, JP,7-230165,A, JP,8-62834,A, JP,9-54432,A, JP,9-5988,A, a U.S. Pat. No. 5405720 number, said 5360692 numbers, said -- No. 5529881 -- said -- No. 5296330 -- said -- No. 5436098 -- said -- No. 5576143 -- said -- a surfactant No. 5294511 and given [this] in No. 5824451 can be mentioned, and the surfactant of the following marketing can also be used as it is. As a surfactant of marketing which can be used, for example, EFUTOPPU EF301 and EF303, (made in new Akita Chemicals), Fluorad 430 and FC 431 (Sumitomo 3M make), the megger fucks F171, F173, F176, F189, and R08 (Dainippon Ink make), A fluorochemical surfactant or silicon system surfactants, such as Sir chlorofluocarbon S-382, SCs 101, 102, 103, 104, 105, and 106 (Asahi Glass Co., Ltd. make), and Troysol S-366 (made in Troy Chemical), can be mentioned. Moreover, polysiloxane polymer KP-341 (Shin-Etsu Chemical Co., Ltd. make) can be used as a silicon system surfactant.

[0104] The loadings of a surfactant are usually 0.01 % of the weight - 1 % of the weight preferably on the basis of the solid content in the constituent of this invention 0.001 % of the weight to 2% of the weight. You may add independently and these surfactants can also be added in some combination. As a surfactant which can be used besides the above Specifically The polyoxyethylene lauryl ether, polyoxyethylene stearylether, Polyoxyethylene alkyl ether, such as the polyoxyethylene cetyl ether and the polyoxyethylene oleyl ether Polyoxyethylene alkyl aryl ether, such as the polyoxyethylene octyl phenol ether and the polyoxyethylene nonyl phenol ether Polyoxyethylene polyoxypropylene block copolymers Sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, Sorbitan fatty acid esters, such as sorbitan monooleate, sorbitan trioleate, and sorbitan tristearate Polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, The Nonion system surfactants, such as polyoxyethylene sorbitan fatty acid ester, such as polyoxyethylenesorbitan monostearate, polyoxyethylene sorbitan trioleate, and polyoxyethylene sorbitan tristearate, etc. can be mentioned. The loadings of other surfactants of these are usually below 1 weight section preferably below 2 weight sections per solid content 100 weight section in the constituent of this invention.

[0105] [5] The positive type photoresist constituent of this invention contains the (C) partially aromatic solvent. (C) as a component -- a chain-like ketone -- at least -- a kind (solvent of A group), lactic-acid alkyl, alkoxy alkyl propionate, acetic ester, and propylene glycol monoalkyl ether -- at least -- the partially aromatic solvent of a kind (solvent of B group) and/or gamma-butyrolactone, ethylene carbonate, and propylene carbonate which contains a kind (solvent of C group) at least -- it is . That is, as a (C) component, the combination of the solvent of A group and the solvent of B group, the combination of the solvent of A group and the solvent of C group, and the combination of the solvent of A group, the solvent of B group, and

the solvent of C group are used.

[0106] A development defect is mitigable with the combination of the solvent of A group, and the solvent of B group. With the combination of the solvent of A group, and the solvent of C group, generating of the particle in the passage of time of this solution can also be controlled further, namely, generating of the particle at the time of resist constituent solution preparation and resist liquid excellent in stability with the passage of time can be offered. Furthermore, the sensibility fluctuation by the passage of time can also be prevented. With the combination of the solvent of A group, the solvent of B group, and the solvent of C group, the stability with the passage of time which mitigated the development defect is excellent, and a resist constituent also with little sensibility fluctuation by the passage of time can be offered.

[0107] As a chain-like ketone, heptanone, such as 2-heptanone, 3-heptanone, and 4-heptanone, octanone, etc. can be mentioned preferably, and especially 2-heptanone is desirable. As lactic-acid alkyl, methyl lactate and ethyl lactate can be mentioned preferably. As alkoxy alkyl propionate, 3-ethoxyethyl propionate, 3-methoxymethyl propionate, 3-methoxy ethyl propionate, and 3-ethoxy methyl propionate can be mentioned preferably. As acetic ester, butyl acetate, pentyl acetate, and acetic-acid hexyl can be mentioned preferably, and it is butyl acetate more preferably. As propylene glycol monoalkyl ether, propylene glycol monomethyl ether and the propylene glycol monoethyl ether can be mentioned preferably.

[0108] The amount of the solvent used of A group is usually 30 % of the weight or more to all solvents, and is 50 % of the weight or more more preferably 40% of the weight or more. Spreading nature may be inferior in it being less than 30 % of the weight. The amount of the solvent used of B group is usually 5 – 70 % of the weight to all solvents, and is 15 – 50 % of the weight more preferably ten to 60% of the weight. If there is less amount of the solvent used of B group than the above-mentioned range, the addition effectiveness will fall, and if 70 % of the weight is exceeded, the problem of spreading nature deteriorating may arise. The operating weight ratio of the solvent of C group has 0.1 – 25 desirable % of the weight to all solvents, and its 1 – 20 % of the weight is more desirable, and it is 3 – 15% more preferably. Preservation stability may be bad if the addition effectiveness may not be acquired if there is less amount of the solvent used of C group than the above-mentioned range, and 25 % of the weight is exceeded. Although the partially aromatic solvent of this invention has especially the desirable thing consisted only of the above-mentioned specific solvent, it may contain other solvents in the range which does not bar the effectiveness of this invention. Generally other solvents are 10 or less % of the weight preferably 20 or less % of the weight among a partially aromatic solvent. As other solvents, propylene-glycol-monomethyl-ether acetate, Propylene glycol monoalkyl ether acetate, such as propylene glycol monoethyl ether acetate Propylene glycol monoalkyl ether carboxylate, ethylene glycol monomethyl ether, Ethylene glycol monoalkyl ether, such as ethylene glycol monoethyl ether Ethylene glycol monoalkyl ether acetate, such as ethylene glycol monomethyl ether acetate and ethylene glycol monoethyl ether acetate Pyruvic-acid alkyl ester, such as methyl pyruvate and pyruvic-acid ethyl, N-methyl pyrrolidone, N,N-dimethylacetamide, dimethyl sulfoxide, etc. are mentioned.

[0109] In this invention, it is desirable to dissolve the solid content of the resist constituent containing each above-mentioned component in the above-mentioned partially aromatic solvent three to 25% of the weight as solid content concentration, it is 5 – 22 % of the weight more preferably, and is 7 – 20 % of the weight still more preferably.

[0110] As a desirable combination of the partially aromatic solvent in this invention 2-heptanone + propylene

glycol monomethyl ether, 2-heptanone + ethyl lactate, 2-heptanone + 3-ethoxyethyl propionate, 2-heptanone + gamma-butyrolactone, 2-heptanone + ethylene carbonate, 2-heptanone + propylene carbonate, 2-heptanone + propylene-glycol-monomethyl-ether + gamma-butyrolactone, 2-heptanone + ethyl lactate + gamma-butyrolactone, 2-heptanone + 3-ethoxyethyl propionate + gamma-butyrolactone, 2-heptanone + propylene-glycol-monomethyl-ether + ethylene carbonate, 2-heptanone + ethyl lactate + ethylene carbonate, 2-heptanone + 3-ethoxyethyl propionate + ethylene carbonate, 2-heptanone + propylene-glycol-monomethyl-ether + propylene carbonate, 2-heptanone + ethyl lactate + propylene carbonate, 2-heptanone + 3-ethoxyethyl propionate + propylene carbonate, They are 2-heptanone + butyl lactate and 2-heptanone + butyl lactate + gamma-butyrolactone, 2-heptanone + butyl lactate + ethylene carbonate, and 2-heptanone + butyl lactate + propylene carbonate.

[0111] Still more preferably 2-heptanone + propylene-glycol-monomethyl-ether + gamma-butyrolactone, 2-heptanone + ethyl lactate + gamma-butyrolactone, 2-heptanone + 3-ethoxyethyl propionate + gamma-butyrolactone, 2-heptanone + propylene-glycol-monomethyl-ether + ethylene carbonate, 2-heptanone + ethyl lactate + ethylene carbonate, 2-heptanone + 3-ethoxyethyl propionate + ethylene carbonate, 2-heptanone + propylene-glycol-monomethyl-ether + propylene carbonate, 2-heptanone + ethyl lactate + propylene carbonate, 2-heptanone + 3-ethoxyethyl propionate + propylene carbonate, They are 2-heptanone + butyl lactate + gamma-butyrolactone, 2-heptanone + butyl lactate + ethylene carbonate, and 2-heptanone + butyl lactate + propylene carbonate.

[0112] The positive type photoresist constituent of this invention can be made to contain the compound which promotes the solubility over an acidolysis nature lysis inhibition compound, a color, a plasticizer, a photosensitizer, and a developer further if needed.

[0113] Such a positive type photoresist constituent of this invention is applied on a substrate, and forms a thin film. The thickness of this paint film has desirable 0.2–1.2 micrometers. In this invention, inorganic [commercial] or an organic antireflection film can be used as occasion demands.

[0114] As antireflection film, inorganic membrane types, such as titanium, a titanium dioxide, titanium nitride, chromic oxide, carbon, and alpha-silicon, and the organic membrane type which consists of an extinction agent and a polymer ingredient can use. The former needs a facility of a vacuum evaporation system, a CVD system, a sputtering system, etc. for film formation. As organic antireflection film, for example The condensation product of a diphenylamine derivative given in JP,7-69611,B, and formaldehyde denaturation melamine resin, The thing, the maleic-anhydride copolymer given in a U.S. Pat. No. 5294680 number, and the reactant of a diamine mold extinction agent which consist of alkali fusibility resin and an extinction agent, The thing containing a resin binder given in JP,6-118631,A, and a methylol melamine system heat cross linking agent, The acrylic resin mold antireflection film which has a carboxylic-acid radical, an epoxy group, and an extinction radical given in JP,6-118656,A in the same intramolecular, What consists of a methylol melamine given in JP,8-87115,A and a benzophenone system extinction agent, the thing which added the low-molecular extinction agent to polyvinyl alcohol resin given in JP,8-179509,A are mentioned. Moreover, DUV30 series by BURYUWA Saiensu-Sha, AC-2 of DUV-40 series and the product made from SHIPURE, AC-3, etc. can also be used as organic antireflection film.

[0115] On a substrate (example: silicon / diacid-ized silicon covering) which is used for manufacture of a precision integrated circuit device, the above-mentioned resist liquid can be exposed through a

predetermined mask after spreading by the suitable methods of application, such as a spinner and a coating machine, (on the substrate which was able to prepare the above-mentioned antireflection film as occasion demands), and a good resist pattern can be obtained by developing negatives by performing BEKU. As an exposure light, it is light with a wavelength of 150nm – 250nm preferably here. Specifically, a KrF excimer laser (248nm), an ArF excimer laser (193nm), F2 excimer laser (157nm), an X-ray, an electron beam, etc. are mentioned.

[0116] As a developer, a sodium hydroxide, a potassium hydroxide, a sodium carbonate, Inorganic alkali, such as a sodium silicate, a meta-sodium silicate, and aqueous ammonia Primary amines, such as ethylamine and n propylamine, diethylamine, Tertiary amines, such as secondary amines, such as G n butylamine, triethylamine, and methyl diethylamine Alcoholic amines, such as dimethylethanolamine and triethanolamine, Alkaline water solutions, such as annular amines, such as quarternary ammonium salt, such as tetramethylammonium hydroxide and tetraethylammonium hydroxide, a pyrrole, and PIHERIJIN, can be used. Furthermore, alcohols and a surfactant can also be used for the alkaline above-mentioned water solution, carrying out suitable amount addition.

[0117]

[Example] Hereafter, although an example explains this invention still more concretely, this invention is not limited to the following examples.

[0118] The synthetic norbornene of resin (1), tert-butyl acrylate, and a maleic anhydride were taught to the reaction container by the mole ratio 40/20/40, it dissolved in the methyl ethyl ketone, and the solution of 60 % of the weight of solid content was prepared. This was heated at 60 degrees C under the nitrogen air current. the place by which reaction temperature was stabilized — the Wako Pure Chem radical initiator V-601 — one-mol% — the reaction was made to start in addition After heating for 10 hours and diluting a reaction mixture with a methyl ethyl ketone twice, it supplied to a lot of tert-butyl methyl ether, and white fine particles were deposited. Filtration ejection of the fine particles which deposited was carried out, and the resin (1) which is desiccation and the specified substance and which was illustrated previously was obtained. When the molecular-weight analysis by GPC of the obtained resin (1) was tried, it was 15300 (weighted mean) in polystyrene conversion. Moreover, the presentation of resin (1) was 38/17/45 in the mole ratio from the NMR spectrum about the norbornene / acrylic-acid t-butyl ester / maleic anhydride of this invention. Resin (2) – (15) illustrated previously was hereafter compounded by the same approach as a synthetic example (1). The presentation ratio of resin and weight average molecular weight (Mw) are shown in Table 1.

[0119]

[Table 1]

表 1

樹脂	加減成分類	酸分解アク リレート	酸無水物	第4成分	Mw
2	38	16	46		14700
3	36	19	45		14900
4	37	10/7	46		15600
5	32	28	40		13800
6	34	18	48		13300
7	36	15	49		12800
8	32	20	48		14400
9	34	17	49		15100
10	30	15/10	45		13000
11	38	14/6	44		14800
12	35	16	46	3	8900
13	30	15	51	4	13000
14	35	16	40	9	14800
15	34	15	43	8	13700

[0120] Examples 1-18 and example of a comparison (preparation and evaluation of a positive type photoresist constituent) The resin (shown in the following table 2) compounded in the above-mentioned synthetic example, respectively 2g, after blending 110mg of photo-oxide generating agents and 5mg of organic base nature compounds shown in Table 2, and 5mg of surfactants and dissolving in the (C) partially aromatic solvent of 10 % of the weight of solid content which comes out of comparatively and which is shown in Table 2, respectively, it filtered by the 0.1-micrometer microfilter and the positive-resist constituent of examples 1-18 was prepared. Moreover, the positive-resist constituent was prepared like the above except using the above-mentioned resin, photo-oxide generating agent, and solvent which were shown in Table 2 as an example 1 of a comparison.

[0121] As a solvent, it is S1:2-heptanone S2:octanone S3:ethyl lactate S4:butyl-acetate S5:propylene-glycol-monomethyl-ether S6:ethoxy-ethyl-propionate S7:gamma-butyrolactone S8:ethylene carbonate S9:propylene carbonate S10:propylene-glycol-monomethyl-ether acetate [0122]. As a surfactant, it is the W-1:megger fuck F176 (Dainippon Ink make) (fluorine system).

W-2: Megger fuck R08 (Dainippon Ink make) (a fluorine and silicone system)

W-3: Polysiloxane polymer KP-341 (Shin-Etsu Chemical Co., Ltd. make)

W-4: Polyoxyethylene nonylphenyl ether W-5 : Troysol S-366 (made in Troy Chemical)

[0123] As an organic base nature compound, it is 1:DBU (1, 8-diazabicyclo [5.4.0]-7-undecene).

2:4-DMAP (4-dimethylaminopyridine)

3: TPI (2, 4, 5-triphenyl imidazole)

*****.

Resin (R): The terpolymer (IV) currently compounded in the example 3 of JP,10-130340,A and (R2=t-butyl) were used.

[0124]

[Table 2]

表2

实施例	(A) 樹脂成分	(B) 光酸発生剤	(C) 溶 剤	(E) 界面 活性剤	(D) 有機塩基 化合物
1	樹脂(1)	PAG4-50	S1/S3=75/25	5	1
2	樹脂(2)	PAG4-5	S1/S6=40/60	4	2
3	樹脂(3)	PAG6-27	S1/S7=80/20	3	3
4	樹脂(4)	PAG3-5	S1/S8=90/10	2	2
5	樹脂(5)	PAG4-7	S1/S9=88/12	1	1
6	樹脂(6)	PAG4-39	S1/S5=50/50	2	2
7	樹脂(7)	PAG4-5/PAG3-5=2/1	S2/S6=78/22	3	1
8	樹脂(8)	PAG4-6	S1/S3/S7=70/25/5	3	2
9	樹脂(9)	PAG3-21	S1/S3/S8=75/20/5	5	3
10	樹脂(10)	PAG4-35	S1/S3/S9=72/20/8	5	3
11	樹脂(11)	PAG7-4	S2/S7=90/10	4	3
12	樹脂(12)	PAG3-5/PAG4-7=1/3	S2/S6/S9=77/19/4	3	2
13	樹脂(13)	PAG4-36	S1/S6/S7=70/26/4	2	1
14	樹脂(14)	PAG4-35/PAG7-3=5/5	S1/S6/S8=68/28/4	1	2
15	樹脂(15)	PAG4-37	S1/S6/S9=68/27/5	2	3
16	樹脂(1)	PAG4-50/PAG6-27=5/5	S1/S7/S8=65/30/5	3	1
17	樹脂(7)	PAG4-18	S1/S7/S9=60/32/8	5	2
18	樹脂(1)	PAG4-5	S1/S3/S8=70/25/5	-	-
比較例					
1	樹脂(R)	PAG4-5	S10	-	-
2	樹脂(R)	PAG4-5	S1	-	-

[0125] (Evaluation trial)

[Development defect] :6 inch Bare Each resist film was applied to 0.5 micrometers on Si substrate, and 140 degrees C dried for 60 seconds with the vacuum adsorption equation hot plate. Next, after exposing through the test mask of 0.35-micrometer contact hole pattern (Hole Duty ratio = 1:3) by the ArF excimer laser stepper (ArF exposure machine 9300 by the ISI company), exposure afterbaking was performed for 90 seconds at 155 degrees C. It rinsed for 30 seconds after the paddle development for 60 seconds, and with pure water by TMAH (tetramethylammonium hydroxide water solution) 2.38% of the weight succeedingly, and spin desiccation was carried out. In this way, the primary data value measured and acquired [number / of development defects] by KLA-2112 Made from a KEERUE ten call opportunity in the obtained sample was made into the number of development defects.

[0126] [-- the number of particle -- passing -- the time -- number of increments] of the particle after preservation -- : -- the number of particle in liquid after leaving it for one week at 23 degrees C immediately after preparation (particle initial value) about the positive type photoresist constituent solution (coating liquid) prepared as mentioned above (the number of particle after the passage of time) was counted at the

Rion make and a particle counter. The number of the increments in particle calculated with particle initial value by - (the number of particle after the passage of time) (particle initial value) was evaluated. In addition, particle counted the number of the particle 0.25 micrometers or more in 1ml of resist constituent liquid.

[0127] [sensibility fluctuation before and behind preservation with the passage of time]: the positive type photoresist constituent solution adjusted above on the silicon wafer -- spreading -- and 140 degrees C was painted by 0.20-micrometer thickness. [for 90 seconds] In this way, it exposed, loading an ArF excimer laser stepper (ArF exposure machine 9300 by the ISI company) with a resolution mask for the obtained wafer, and changing light exposure. the tetramethylammonium hydronalium oxide developer (2.38 % of the weight -- for 60 seconds -- developing negatives -- distilled water -- a rinse -- it dried and the pattern was obtained.) after heating 155 degrees C for 90 seconds in a clean room after that Thus, the sensibility (the same appraisal method as the above) after evaluating the sensibility (let the minimum light exposure reproducing 0.15-micrometer Rhine and a tooth-space pattern be sensibility) immediately after preparation of a positive type photoresist constituent solution (coating liquid) and leaving the above-mentioned constituent solution for one week at 4 degrees C was evaluated, and the following type estimated sensibility rate of change.

sensibility rate-of-change (%) =
$$\frac{((\text{sensibility before preservation}) - (\text{sensibility after preservation}))}{(\text{sensibility before preservation})} \times 100$$
 -- these evaluation results are shown in Table 3.

[0128]

[Table 3]

表3

実施例	現像欠陥数	パーティクル 初期値	パーティクル 増加数	感度変動率 (%)
1	10	5	10	0
2	10	6	10	2
3	10	5	10	1
4	28	5	<5	0
5	30	6	<5	3
6	10	5	11	1
7	11	5	12	3
8	9	5	5	0
9	10	<5	5	1
10	9	<5	<5	2
11	10	<5	11	1
12	11	5	5	1
13	9	<5	<5	1
14	10	<5	<5	2
15	9	<5	<5	1
16	9	<5	<5	1
17	11	<5	<5	2
18	11	<5	<5	1
比較例 1	113	105	1000	17
比較例 2	220	210	1150	13

[0129] As shown in the above-mentioned table 3, the positive type photoresist constituent of this invention showed the engine performance which was excellent in all evaluation criteria.

[0130]

[Effect of the Invention] This invention can offer the positive type photoresist constituent which generating of a development defect can be mitigated, can prevent generating of the particle at the time of melting solid content to a solvent, or the time of preservation with the passage of time, and can prevent fluctuation of the sensibility by preservation with the passage of time in manufacture of a semiconductor device.

[Translation done.]